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MEASUREMENT OF THE APPARENT FLUIDITY OF DISPERSIONS OF CELLULOSE IN CUPRAMMONIUM SOLUTION

By Ralph T. Mease

ABSTRACT

The importance of the cuprammonium fluidity test for the indication of fundamental change in cellulose, particularly in the earlier stages of degradation, is quite generally recognized. Without special equipment and technique, however, the test is difficult to perform. It is the object of this paper to describe relatively simple equipment and technique found practical for measurement of the apparent fluidity of dispersions of cellulose in cuprammonium solution.

Directions are given for the preparation and storage of the cuprammonium solution; for the construction and calibration of viscometers; for the dispersion of cellulose in the cuprammonium solution; and for the measurement of the fluidity of the dispersion. Some of the difficulties which arise in precise measurements are indicated, and data illustrating the duplicability of results are presented.

CONTENTS

	Page
I. Introduction	271
II. Cuprammonium solution	272
III. The viscometer and its construction	277
IV. Calibration of viscometer	279
V. Duplicability of viscometers	282
VI. Procedure for the determination of the fluidity of cellulose dispersions	282
VII. Duplicability of fluidity measurements	283

I. INTRODUCTION

It has been observed that the quality of cellulose is indicated by its tensile strength, copper number, methylene blue absorption, and the apparent fluidity of its dispersions in standard cuprammonium solution.[1] The apparent fluidity of such dispersions has been found to be a much more sensitive and precise measure of the changes in the quality of cellulose brought about by the action of light, heat, laundering, and chemicals, particularly in the early stages, than is afforded by the other methods.

Although cellulose can be dispersed in certain salt solutions [2 3 4] and in concentrated mineral acids,[5 6] considerable hydrolysis of the

[1] Charles Dorée, Methods of Cellulose Chemistry (Chapman & Hall, Ltd., London 1933).

[2] H. E. Williams, *The action of thiocyanates on cellulose*, J. Soc. Chem. Ind. **40**, 221T (1921).

[3] P. P. von Weimarn, *Bemerkungen über meine Methode der Dispersion von Zellulose in konzentrierten wässerigen Lösungen neutraler Salze*, Kolloid-Z. **29**, 197 (1921).

[4] P. P. von Weimarn, *Ueber die Eigenschaften der "reinen" Zellulose als Kolloid*, Kolloid-Z. **44**, 212 (1928).

[5] C. E. Guignet, *Cellulose colloids, soluble et insoluble: Constitution du Papier Parchemin*, Compt. rend. **106**, 1258 (1888).

[6] R. Willstätter and L. Zechmeister, *Zur Kenntnis der Hydrolyse von Cellulose*, Ber. deut. chem. Ges. **46**, 2401 (1913).

cellulose may take place. Cuprammonium solution, however, appears to come closer than any other known dispersing agent to being a true physical solvent for cellulose.[7] Although cellulose regenerated from cuprammonium solution is in the hydrated form, there is evidence which indicates that it has undergone less change in the process of solution and regeneration than when other available dispersing agents are used. Cuprammonium solution is therefore regarded by many as the best medium for the examination of cellulose in a highly dispersed state.

The principles upon which fluidity measurements of cellulose solutions are based are adequately described elsewhere.[8] Considerable difficulty, however, is met in duplicating fluidity measurements. The preparation, preservation, and handling of the unstable cuprammonium solution; the construction and calibration of viscometers; the dispersion of high-grade cellulose; and the adequate control of temperature while the measurements are made, require special equipment and technique. The reliability of the results obtained is determined by the precautions taken in the experimental details, the omission of any of which may lead to erroneous results or complete failure.

It is the purpose of this paper to describe simple laboratory manipulations; convenient and inexpensive equipment which is readily constructed and is suitable for the measurements; and to present data obtained under practical working conditions to illustrate the precision obtained.

II. CUPRAMMONIUM SOLUTION

Cuprammonium solutions of different concentrations of copper and ammonia have been used for the dispersion of cellulosic materials.[9] The ability to disperse cellulose and the flow characteristics of the resulting dispersions depend upon these concentrations. Solutions relatively high in ammonia content are better dispersing media than similar solutions of lower ammonia concentration.[10]

A solution containing 240 ± 5 g of ammonia (NH_3) and 15 ± 0.1 g of copper per 1,000 ml is satisfactory for the dispersion of cellulose of different forms, including cotton fibers which have not been subjected to any drastic chemical processing. Dispersions of high-grade cotton have fluidities as low as 1 to 2 rhes [11] in a 0.5-percent solution and are relatively difficult to disperse. The regenerated celluloses, and celluloses modified by bleaching, heating, laundering, or industrial processing are more readily dispersed. A solution of lower ammonia concentration could be used to disperse these materials.

Figure 1 is a diagram of the equipment for the preparation of the cuprammonium solution. The Pyrex-glass cylinder, 13, approximately

[7] Alfred J. Stamm, Colloid Chemistry of Cellulosic Materials, U. S. Dept. of Agriculture, Misc. Pub. **240**, p. 26 (1936).

[8] D. A. Clibbens and A. Geake, *The measurement of the fluidity of cotton in cuprammonium solution*, J. Textile Inst. **19**, T77 (1928).

[9] E. K. Carver and Harold Folts, *The plasticity of cellulose in cuprammonium hydroxide*, J. Am. Chem. Soc. **47**, 1430 (1925).

[10] The Effect of Variations in Ammonia Concentration on the Fluidity of 0.5-Percent Cellulose Solutions. Appendix III. The Viscosity of Cellulose Solutions. Dept. Sci. Ind. Research (Brit.) Comm. Repts. (1932).

[11] According to the definition by the Society of Rheology, a "rhe" is the unit of fluidity in the cgs system. The fluidity of a simple liquid is the reciprocal of the viscosity. It must be recognized that dispersions of cellulose in cuprammonium solution do not behave like simple liquids, since the rate of shear is not proportional to the shearing stress, and that the terms "fluidity" and "rhe" as applied here are not in strict accord with the conventions of rheology. We are concerned here with what may be called "apparent fluidity" as indicated in the title.

29 cm in diameter and 29 cm deep, rests upon the circular brass plate, 12, and is covered by the iron cover, 11. This cover is held in place by the bolts, 15, and a tight seal is obtained with the rubber gasket, 10. The cover is fitted with the iron air-intake tube, 7, a bearing for the iron stirrer shaft, 9, a capillary exhaust tube and rubber stopper, 22, and the siphon, 14. The end of the shorter arm of the siphon is placed 1 to 2 cm above the bottom of the glass cylinder. The upturned end, 16, of the air-intake tube passes through a hole in the hollow crossarm of the stirrer and is fitted with an iron collar serving as a bearing for the rotating stirrer. The cylinder thus fitted is placed in the double-walled sheet-copper container, 5, with rock wool between the walls for thermal insulation. The air-intake tube is connected with the gas-washing bottle, 4, containing concentrated ammonium hydroxide of specific gravity not over 0.90, and with the differential manometer, 3, and the trap containing glass wool through which the air is introduced at 1. The manometer and capillary serve

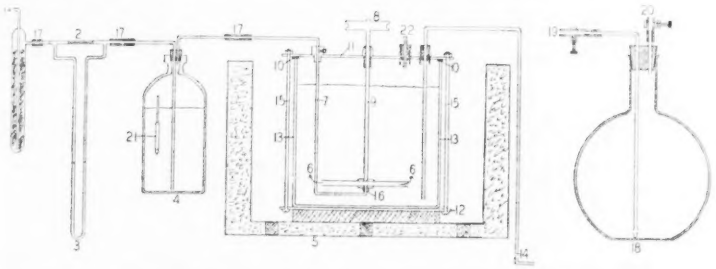

FIGURE 1.—*Equipment for preparing standard cuprammonium solution.*

1, Air inlet; 2, capillary flow regulator; 3, manometer; 4, reservoir for ammonia; 5, insulated container for ice; 6, hollow arm of stirrer; 7, iron tubing; 8, pulley; 9, shaft; 10, crude-rubber gasket; 11, iron plate; 12, brass plate; 13, Pyrex-glass cylinder, 12 by 12 inches; 14, siphon; 15, iron bolts; 16, bearing for stirrer; 17, rubber connections; 18, 12-liter Pyrex flask; 19 and 20, rubber connections with pinch clamps; and 21, hydrometer.

as a flowmeter to facilitate the regulation of the rate of flow of air. A rate of 10 liters per hour, at the pressure necessary to force it through the system when charged as directed below, is satisfactory.

The length of the capillary convenient for constructing the flowmeter to deliver approximately 10 liters of air per hour at room temperature can be calculated with sufficient accuracy for the purpose by arbitrarily choosing a convenient difference in the level of the water columns in the manometer, and using the equation

$$l = 0.76\ hr^4, \qquad (1)$$

where h is the difference in the water levels, r the radius, and l the length of the capillary in centimeters.

The space between the glass cylinder and the inner wall of the insulated copper container is packed with ice. The cylinder, 13, is charged with 15 liters of ammonium hydroxide solution of specific gravity 0.88 to 0.90. The stirrer is rotated at about 30 rpm and 15 g of cane sugar followed by 900 g of precipitated copper powder are added. The opening in the cover is then closed with the rubber stopper and capillary tube, 22. The wash bottle, 4, is charged with 2 liters of ammonium hydroxide of the same concentration as that used to charge

the cylinder. The flow of air is then started. If, during the operation the ammonium hydroxide solution in the wash bottle changes so that its specific gravity becomes greater than 0.90, it should be replaced or some gaseous ammonia added. The change in concentration of this solution can conveniently be observed by temporarily stopping the air flow and observing the reading on the hydrometer, 21. The stirring and the flow of air are continued until tests show that the concentration of copper is a little more than 15 g per liter.

For the purpose of observing the change in concentration of dissolved copper, the stirring is stopped and the undissolved powdered copper permitted to settle for a few minutes. A portion of the solution is drawn out by means of a pipette fitted with a rubber bulb and 5 ml of it is placed in a 50-ml Nessler tube and diluted to the mark with water. Five ml of a copper sulfate solution containing 15 g of copper (59 g of $CuSO_4.5H_2O$) per liter is placed in a second Nessler tube, 10 ml of concentrated ammonium hydroxide is added, and the mixture diluted with sufficient water to fill the tube to the mark. When the color of the copper solution taken from the cylinder is just noticeably deeper than that prepared from the copper sulfate solution, the stirring and air flow are stopped and the mixture is allowed to settle overnight.

A 12-liter Pyrex flask, 18, is provided with rubber stopper, connections, and clamps as shown. The air in it is displaced by nitrogen by passing the gas into the flask through the opening, 20, and exhausting through 19. After the air has been displaced, the openings are closed by means of the clamps and the flask is weighed. The cuprammonium solution is then transferred from the cylinder in which it is prepared to the flask by connecting it with the siphon at 14. The flow is started by air pressure applied through the tube, 22, after opening the clamps, 19 and 20, and continued until the flask has been filled within about 10 cm of the stopper, when the flow is stopped by closing the clamp at 19. The clamp at 20 is also closed to prevent air from entering the flask, which is packed in ice or placed in a refrigerator and allowed to stand overnight to permit any undissolved copper to settle. The solution must be kept cool and in a closed container at all times to prevent the escape of ammonia and reaction with air.

About 100 ml of the solution is removed from the flask for analysis by attaching a glass tube to the rubber tube at 19 and one at 20, through which a stream of nitrogen can be forced when the clamps are released. This portion is also kept on ice. The clamps are closed and the flask and its contents weighed.

A 5-ml specimen of the ice-cold solution is pipetted into a 300-ml Erlenmeyer flask containing at least 50 ml of standard approximately 2 *N* sulfuric acid. The solution is added slowly with the tip of the pipette touching the bottom of the flask, which is cooled in ice water. A few drops of methyl red indicator are added and the sulfuric acid not neutralized by the cuprammonium solution is titrated with standard approximately normal sodium hydroxide solution. A second 5-ml portion of the cuprammonium solution is placed in a 250-ml beaker, diluted with about 20 ml of distilled water, acidified with sulfuric acid, and the copper determined by electrodeposition.[12]

[12] W. F. Hillebrand and G. E. F. Lundell: Applied Inorganic Analysis; with Special Reference to th Analysis of Metals, Minerals, and Rocks, p. 197 (J. Wiley & Sons, New York, N. Y., 1929).

The cuprammonium solution prepared in the manner described contains a little more copper and ammonia than required for use and needs to be diluted with ammonium hydroxide of the required concentration. The volume of the cuprammonium solution to be removed and replaced by an equal volume of ammonium hydroxide may be calculated by the formula:

$$V=\frac{(\mathrm{Cu}_p-15)(W_p-W_e)}{\rho \mathrm{Cu}_p} \tag{2}$$

and the concentration of the ammonia solution to be added is:

$$C_{\mathrm{NH_3}}=\frac{248\ \mathrm{Cu}_p-51(V_{\mathrm{H_2SO_4}}\cdot N_{\mathrm{H_2SO_4}}-V_{\mathrm{NaOH}}\cdot N_{\mathrm{NaOH}})}{\mathrm{Cu}_p-15}, \tag{3}$$

where

Cu_p=the number of grams of copper in 1 liter of the solution as prepared.

W_e=weight in grams of the flask filled with nitrogen.

W_p=weight in grams of the flask filled with the solution as prepared.

ρ=density of the solution in grams per ml. If the directions for preparing the solution are followed, this may be taken as 0.93, or the density of the solution adjusted to the proper concentration for use.

$N_{\mathrm{H_2SO_4}}$=normality of the standard sulfuric acid solution.

N_{NaOH}=normality of the standard sodium hydroxide solution.

V_{NaOH}=volume in milliliters of the standard sodium hydroxide required for the titration.

$V_{\mathrm{H_2SO_4}}$=volume in milliliters of the standard sulfuric acid used.

V=volume in milliliters of the prepared cuprammonium solution to be removed from the flask and replaced by an equal volume of ammonium hydroxide solution of concentration $C_{\mathrm{NH_3}}$ g of ammonia ($\mathrm{NH_3}$) per liter.

The solution to be added is prepared from concentrated ammonium hydroxide (sp gr 0.88 or less). Five ml of the concentrated ammonia solution is analyzed for ammonia content in the same manner described for the titration of ammonia in the prepared cuprammonium solution. A measured volume, V_m, in milliliters equal to or greater than V (formula 2) is taken to adjust to the concentration $C_{\mathrm{NH_3}}$ (formula 3). The volume of water, $V_{\mathrm{H_2O}}$, in milliliters to add to this volume is:

$$V_{\mathrm{H_2O}}=\frac{3.4\ V_m\ (T_{\mathrm{H_2SO_4}}\cdot N_{\mathrm{H_2SO_4}}-T_{\mathrm{NaOH}}\cdot N_{\mathrm{NaOH}}}{C_{\mathrm{NH_3}}}-V_m, \tag{4}$$

where $T_{\mathrm{H_2SO_4}}$ and T_{NaOH} are the number of milliliters of standard sulfuric acid and standard sodium hydroxide solutions, respectively, used in the titration. The calculated volume of water is added to the ammonia solution and well mixed in a stoppered bottle.

The volume of solution, V, is removed from the flask in the manner previously described and an equal volume of the ammonia solution prepared is added to that in the flask through opening 19 (fig. 1), care being taken to minimize the loss of ammonia by keeping the

solutions cold. The contents of the flask are well mixed by shaking and permitted to stand, preferably overnight, to permit any powdered copper which may possibly be present to settle. The solution is then transferred to the flask 1 (fig. 2).

Figure 2 is a diagram of equipment designed for storing the supply of cuprammonium solution in an accessible manner. It consists of the 12-liter Pyrex flask, 1, in the cold chamber of a refrigerator, 2, and the Kipp's generator, 3, with the connections shown. A copper tank, 4, in which the flask containing the solution is fastened, may be packed with ice as a precaution against failure of the mechanical refrigeration.

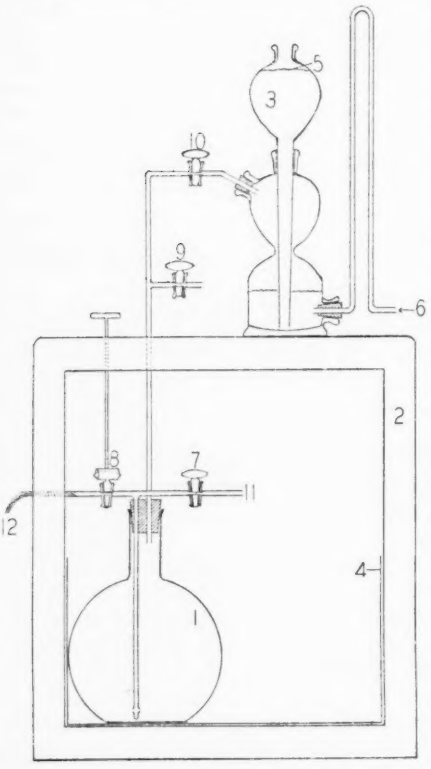

FIGURE 2.—*Refrigerator for storing and delivering cuprammonium solution.*

1, 12-liter Pyrex flask; 2, refrigerator wall; 3, Kipp's generator; 4, copper tank; 5, level of liquid in charged Kipp's generator; 6, inlet for nitrogen; 7, stopcock for filling; 8, stopcock for tapping; 9, stopcock for releasing pressure in flask when filling; 10, stopcock for controlling flow of nitrogen; and 11, filling tube.

The Kipp's generator is charged with nitrogen and a solution of pyrogallol.[13] The pyrogallol solution serves to supply the necessary pressure to deliver the cuprammonium solution when needed and to absorb oxygen which may be in the commercial supplies of nitrogen. The surface, 5, of the pyrogallol solution exposed to the air is covered with a layer of mineral oil to lessen the absorption of atmospheric oxygen.

Preliminary to introducing the solution into the flask, the air in it is displaced by nitrogen. The nitrogen is passed into the system at 6 with stopcocks 10, 8, and 7 opened and 9 closed. After the air has been removed, all the stopcocks are closed and the flow of nitrogen into the Kipp's genererator is continued until the level of the liquid is raised to position 5, when the flow is stopped. To transfer the solution from flask 18, figure 1, to flask 1, figure 2, the tubes 11, figure 2, and 19, figure 1, are connected by means of a rubber tube which is as short as practicable. The clamp at 19 and stopcocks 7 and 9 are opened and the solution is forced into the receiving flask by admitting nitrogen under slight pressure into the first flask through the opening at 20.

[13] Prepared by dissolving 15 g of pyrogallol in 5 to 10 ml of warm water, which is then added to 100 ml of a solution of potassium hydroxide saturated at room temperature.

After the solution has been transferred, stopcocks 7 and 9 are closed. Stopcocks 10 and 8 are opened to remove the solution as needed through the capillary tube 12, which extends through the wall of the refrigerator. Stopcock 8 is fitted with an extension as shown.

After the solution has been adjusted for concentration, it is analyzed once more for ammonia and copper in the manner previously described. The ammonia content of the cuprammonium solution in grams of ammonia per liter is given by the formula

$$3.4\ (V_{H_2SO_4} \cdot N_{H_2SO_4} - V_{NaOH} \cdot N_{NaOH} - 0.157\ Cu_p) \qquad (5)$$

with the symbols used as in the previous formulas.

In addition to the determination of copper and ammonia, the solution is analyzed for nitrogen in the form of nitrates and nitrites [14] with a nitrometer.

If this nitrogen calculated as nitrous acid is more than 0.5 g, or the concentration of ammonia (NH_3) other than 240 ± 5 g, or the copper concentration other than 15 ± 0.1 g per liter of solution, the solution is discarded, or adjusted to the proper concentration, if practicable.

Solutions prepared and stored in the manner described can readily be duplicated and will not change measurably over considerable time. Table 1 gives results of analyses made of a 12-liter lot of solution when first placed in the refrigerator and after approximately 11 months of storage, during which time about 9 liters of the solution was used for making fluidity measurements.

The results of analyses of a second solution prepared to replenish the laboratory supply are also given in table 1, and illustrate the degree of duplicability attainable with ordinary care in the preparation of standard cuprammonium solutions.

TABLE 1.—*Results of analyses of standard cuprammonium solutions indicating the permanency on storage and duplicability of solutions prepared at different times by a standard procedure.*

	Solution 1		Solution 2
	When first made	After 11 months' storage	When first made
Copper (g/liter)	14.96	15.01	15.04
Ammonia (g/liter)	239.8	238.4	240.9
Nitrous acid (g/liter) (nitrometer method)	<0.5%	<0.5%	<0.5%

III. THE VISCOMETER AND ITS CONSTRUCTION

A viscometer for measuring the fluidity of cuprammonium dispersions of cellulose has been described by Clibbens and Geake. An adaptation of the viscometer with accessories is shown in figure 3. The chamber, *A*, of the viscometer is constructed from Pyrex tubing

[14] *Determination of nitrogen of nitrates (and nitrites) by means of the nitrometer.* Standard Methods of Chemical Analysis, third edition, **1**, 353, edited by Wilfred W. Scott (D. Van Nostrand Co., Inc., New York, N. Y., 1922).

of inside diameter 10 ± 0.25 mm. The capillary discharge tube, B, is also of Pyrex with an outside diameter of 6 ± 2 mm and an inside diameter of 0.88 ± 0.02 mm. The markings, M_1 and M_2, on the outside of the wall of the body of the viscometer are spaced at the distances indicated in the figure with respect to the capillary opening.

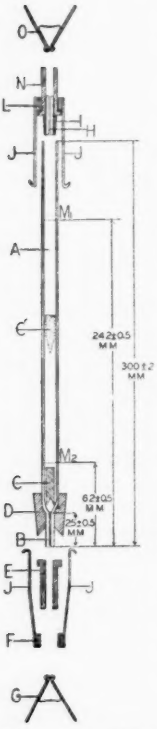

FIGURE 3.—*Viscometer and accessories.*

A, body of viscometer; *B*, capillary discharge tube, 0.88±0.02 mm inside diameter; *C*, steel plunger; *C'*, side view of plunger; *D*, rubber stopper; *E* and *N*, flanged rubber tubes; *O* and *G*, clips; *H*, glass capillary tube; *I*, rubber stopper; *J*, metal hooks to take rubber bands; *F* and *L*, metal collar; and M_1 and M_2, calibration markings.

To construct the viscometer, glass tubing of the dimensions specified is chosen. All indicated dimensions of the viscometer, with the exception of the diameter of the capillary discharge tube, can be determined sufficiently closely by an ordinary scale graduated in millimeters. In practice several capillary tubes may be roughly measured by means of a micrometer and glass rod drawn to a taper, the end of which is slightly less than 0.8 mm. By noting the section of the taper having a diameter of approximately 0.88 mm found by measurement with the micrometer, an approximate measurement of the capillaries can be made by inserting the taper in their ends and noting the depth of insertion. A length of capillary tubing found roughly to have an inside diameter of 0.88 mm is well cleaned by drawing a mixture of nitric and sulfuric acids through the tube, rinsing it with water and drying it with a stream of clean dry air. A more accurate measure of the diameter is then made by drawing sufficient clean mercury into the capillary to fill it for about three-fourths of its length. The length of the mercury column is measured and the mercury transferred to a tared glass vessel and weighed. The diameter of the capillary is then found by calculation thus:

$$\text{diameter in mm}=3.06\sqrt{\frac{g}{h}}, \tag{6}$$

where g is the weight of mercury in grams, and h is the length of the mercury column in centimeters.

A length of capillary tube of the specified diameter is sealed [15] to the large bore-tubing, working glass into the walls of the sealed portion to give sufficient strength to withstand the action of the steel plunger, shown at C and C', which strikes this part of the tube when it is used in effecting dispersion of the cellulose. After sealing, the capillary and large tube forming the body of the viscometer are cut to be a little longer than the indicated dimensions, and the excess lengths of glass ground away on a metal plate with water and carborundum of about 150 mesh. During the grinding the inside of the capillary should be frequently flushed with water to prevent its becoming clogged. The markings M_1 and M_2 are placed by smoking the portion of the tube to be marked, in a gas flame, first marking

[15] H. P. Waran, Elements of Glass-Blowing, chap. 3, on joining tubes (G. Bell and Sons, Ltd., London, 1923).

the tube by a scratch through the carbon layer with the end of one leg of a dividing compass, while the other is set at the end of the capillary discharge tube with the dividers spread the required distance. The mark is then impressed in the glass with a diamond, tungsten-carbide pencil, or file, while the tube is slowly turned in a lathe chuck with the portion of the viscometer clamped in the chuck protected with rubber tape.

Accessories for the viscometer are also illustrated in figure 3. The rubber parts, *E*, *D*, *N*, and *I*, are molded from an uncured rubber compound and vulcanized, or buffed and carved into shape from rubber tubing and stoppers of appropriate size. Carving is facilitated by having the rubber and cutting tools wet with water. *H* is a short length of capillary tubing through which the air and excess liquid are discharged when filling the viscometer. A plunger, *C* and *C'*, made from ¼-inch steel rod with one end wedge-shaped and notched, is provided to agitate the contents when the tubes are filled and rotated end over end. This plunger should weigh 5.6 ± 0.2 g and may be replaced by an equal volume of mercury (see footnote 10) when celluloses are to be tested, which are easily dispersed in the cuprammonium solution. Pinch clamps, *O* and *G*, are provided for closing the rubber fittings on the ends of the charged viscometer.

IV. CALIBRATION OF VISCOMETER

Viscometers for precise work require calibration, since it is impracticable to construct them sufficiently close to specified dimensions. The method of calibration described by Clibbens and Geake, or the graphical method of Higgins [16] [17] [18] [19] may be used.

The method of Clibbens and Geake consists in the determination of the instrumental constants *C* and *K*, by means of the equation

$$F = \frac{C}{\rho\left(t - \frac{K}{t}\right)}, \tag{7}$$

where *F* is the fluidity, in rhes, of a calibrating liquid of predetermined fluidity, *t* is the time, in seconds, of flow of the volume *V*, of liquid contained between the calibration marks M_1 and M_2, and ρ is the density, in grams per cubic centimeter, of the calibrating liquid. For the determination of *C* a liquid of low fluidity is chosen so that the kinetic energy of flow is sufficiently small to be neglected, for the degree of accuracy desired in the measurements. For this purpose Clibbens and Geake use a mixture of water and glycerol of density

[16] W. F. Higgins, *On the methods and apparatus used in petroleum testing.* Nat. Phys. Lab. Collected Researches **11**, part 2, Viscometry, 3 (1914).
[17] Winslow H. Herschel, *Determination of absolute viscosity by short-tube viscometers.* Tech. Pap. BS **9**, (1917) T100.
[18] Winslow H. Herschel, *The standard Saybolt universal viscosimeter.* Proc. Am. Soc. Testing Materials **18**, part 2, 366 (1918).
[19] Eugene C. Bingham, *Recent progress in consistency measurement.* Am. Soc. Testing Materials Symposium on Consistency, New York, N. Y., June 29, 1937.

1.1681 and fluidity of 6.83 rhes at 20° C. The constant, C, is then calculated from eq 8, which follows from eq 7 when $K=0$.

$$C=F\rho t. \tag{8}$$

Two methods for finding K are also given. In the first method, the coefficient of the kinetic-energy correction, m, is taken as 1.12, the entire correction being $1.12\ V/(8\pi lt)$. The constant K of eq 7 is $(1.12V/(8\pi l))C$. In the second method, if t_w is the time of flow for water of fluidity F_w and C has been determined,

$$K=\frac{F_w\rho t_w^2-Ct_w}{F_w\rho}, \tag{9}$$

where ρ may be taken as unity.

In the Higgins method of calibration,

$$\eta=\rho\left(At-\frac{B}{t}\right), \tag{10}$$

where A and B are constants, B/t is the kinetic-energy correction, and by definition η is $1/F$, which is also the viscosity in poises. By comparing eq 7 and 10, it may be shown that $C=1/A$ and, provided K is accurately determined, $K=CB$.

Two or more calibrating liquids may be selected so that their fluidities cover the range of apparent fluidities of the cellulose dispersions to be measured. It is satisfactory to use three liquids, one of fluidity 3 to 5 rhes (viscosity 0.33 to 0.20 poise), another of 46 to 48 rhes (0.0217 to 0.0208 poise) and one of intermediate fluidity, 28 to 30 rhes (0.036 to 0.033 poise). From the experimental data a graph is prepared by plotting $\eta/\rho t$ against $1/t^2$. For viscometers constructed in accordance with the specifications given in section III, using calibrating liquids of the fluidities suggested above, the points representing each of the three calibrating liquids should locate a straight line. The instrumental constant, A, is the intercept of this line on the $\eta/\rho t$ axis (where $1/t^2=0$), and B is the slope of the line. The calibration graph, extended, did not pass through a point obtained for water at 20° C, for any one of the viscometers. Therefore, the relation $K=CB$ does not hold when water is used as one of the calibrating liquids.

Advantages of the Higgins method are that it does not necessitate the determination of V; nor does it involve the dubious assumptions that the kinetic energy correction is negligible for the calibrating liquid of lowest fluidity used; that the coefficient of the kinetic-energy correction has a constant value of 1.12 [20] [21] [22] for capillaries with a trumpet-shaped entrance, and that, when water is used as a calibrating liquid, there is no danger that it may exhibit turbulence or possess properties which cause annoying flow characteristics. In general, it seems safer to use calibrating liquids which cover approximately the same range of fluidities as the solutions to be tested. It has also been found that the Higgins method is the more convenient of the two, both as regards

[20] E. C. Bingham, Fluidity and Plasticity, p. 20. (McGraw-Hill Book Co., New York, N. Y., 1922.)
[21] William Rieman, III, *The value of the Hagenbach factor in the determination of viscosity by the efflux method*, J. Am. Chem. Soc. **50**, 46 (1928).
[22] L. W. Spooner and P. Serex, *A new feature in the calibration of a capillary-tube viscometer*, Physics **6**, 162 (1935).

calibration, and in calculating F (equal to $1/\eta$) from eq 10 rather than from eq 7. Both methods were used in the present work, however, and the differences were never greater than 2 percent. The values shown in figure 6 were obtained by the Higgins method.

Care must be taken in handling the calibrating liquids not to contaminate them or permit change of termperature while making the measurements. A, in figure 5, illustrates a form of vessel suitable for the purpose. It is filled with the calibrating liquid through B, which is then closed with a small stopper and is placed in the constant-temperature bath illustrated in figures 4 and 5 to attain the proper temperature and supported in such a position that the delivery tube C, figure 5, is directly over the opening of the viscometer in position ready for measurements. The viscometer is filled by applying air pressure at H.

The time required for the meniscus of the liquid to travel from the top marking on the viscometer to the bottom one is recorded. From this time of flow, the viscosity of the liquid, the values $1/t^2$ and $\eta\rho t$ previously referred to are calculated.

A thermometer, 1 (fig. 4), with a scale marked in tenths of a degree is provided near the chamber, 2, in which the viscometer, 3, containing the fluid to be measured is shown in position. The chamber, 2, is made from large-bore glass tubing (about 4.5 mm inside diameter), with the lower end consisting of a short section of smaller glass tubing (2.2 mm inside diameter) sealed in the larger and communicating with the exterior of the bath through a large rubber stopper, 4. The upper end of the smaller tube is kept closed when the viscometer is in place by the rubber stopper, D, and the chamber is completely filled with water of the proper temperature from the reservoir, 5, by lifting the long-handled stopper, 7. Observations on the position of the meniscus of the liquid flowing from the viscometer, and thermometer readings are made through the glass window, 8. When the viscometer is to be removed, the chamber, 2, is emptied by opening the pinch clamp, 9, with the upper end of tube, 6, closed.

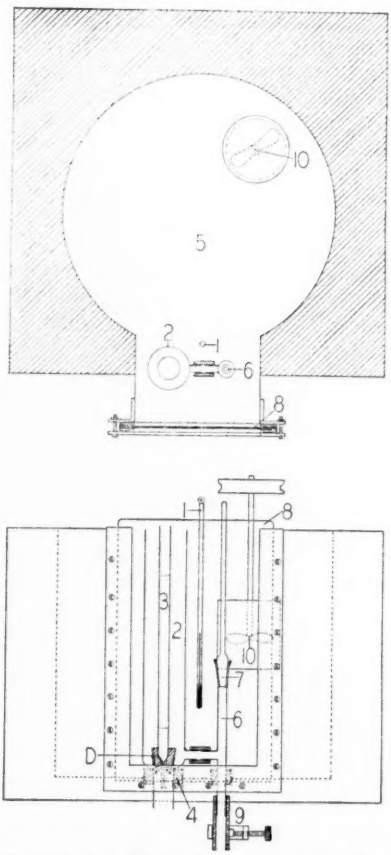

FIGURE 4.—*Water bath for controlling temperature while making measurements*

1, thermometer; 2, glass-walled water jacket for viscometer; 3, viscometer; 4, large rubber stopper; 5, water reservoir; 6, tube for filling water jacket around viscometer; 7, long-handled stopper; 8, glass window 9, rubber tube and pinch clamp; 10, stirrer; and D, rubber stopper supporting viscometer.

When making fluidity measurements at or near room temperature, the temperature of the water in the reservoir and around the viscometer in place for making observations, can readily be kept constant within $\pm 0.05°$ C by adding warm or cold water as needed. Sudden changes in temperature are avoided by using a rather large volume of water in the reservoir which is well insulated and provided with a circulating device, 10.

Liquids used as fluidity standards may change on storage. For this reason it is convenient in practice to calibrate a viscometer carefully and use it exclusively for the accurate redetermination of the fluidity of the reference liquid at the time it is to be used for calibration purposes. Samples of oil of known viscosity for calibration purposes can be obtained from the National Bureau of Standards.

In order to determine the weight of cellulose to place in a viscometer to produce a solution of definite and chosen concentration for the fluidity measurements of cellulose dispersions, the total capacity of the viscometer must be known. The empty viscometer with the steel plunger and connections in place as shown in the photograph in figure 3, is weighed. It is then filled with water in such a manner as to displace all of the air in the instrument. It is wiped dry and again weighed; the difference in these weights in grams at room temperature is taken as the volume L, in milliliters of the viscometer. The amount of cellulose specimen in grams required for a chosen concentration in percent on a dry basis is given by the relation

$$\frac{0.93\ LP}{100-M'} \tag{11}$$

where P is the percentage concentration chosen, and M is the percentage of moisture in the cellulose.

V. DUPLICABILITY OF VISCOMETERS

The duplicability of viscometers when made by a laboratory technician of average ability in glass working is illustrated by results obtained with a group of viscometers which were made and calibrated as described. The capacities differed from 19.20 to 20.66 ml with an average difference from the mean value of 1.3 percent and of the A constants from 0.000452 to 0.000593. Figure 6 presents data which show the duplicability of measurements obtainable with one viscometer, or with different viscometers which exhibit these differences in the A constants. The B constants differed from 0.200 to 0.220. The effect of the kinetic-energy correction, B/t on F is small when liquids of low fluidity are measured but amounts to about 14 percent of the value for F for liquids of fluidity of 45 rhes, which is the upper limit of the range of fluidities in which the viscometers are recommended for use.

VI. PROCEDURE FOR THE DETERMINATION OF THE FLUIDITY OF CELLULOSE DISPERSIONS

When the fluidities of cellulose dispersions are to be determined the viscometer serves as the container for the dispersion of the specimen in the cuprammonium solution.

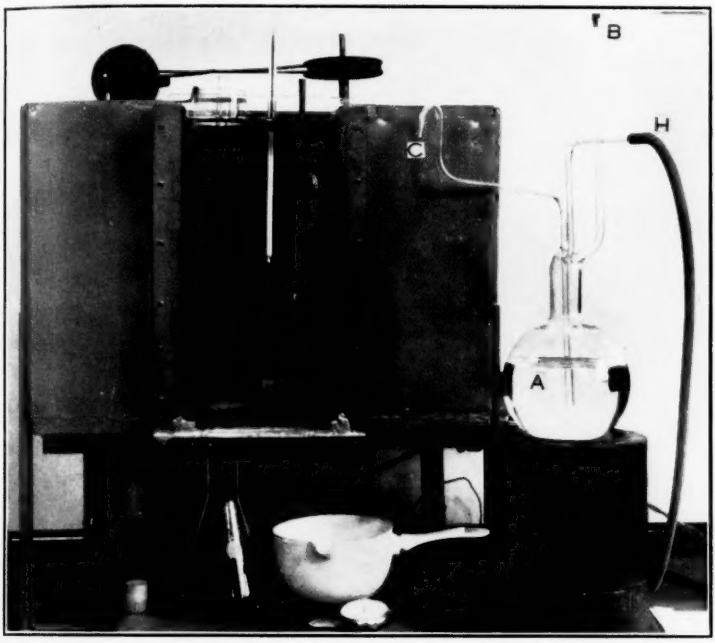

FIGURE 5.—*Constant-temperature bath for controlling the temperature while making flow measurements.*

Special container with calibrating liquid shown at A.

To charge the viscometer with cellulose and cuprammonium solution, the capillary end is closed by means of the clip, collar, and rubber connections *G*, *F*, and *E*, figure 3. The wedge, *C*, is placed in the tube and the tube is nearly half filled with cuprammonium solution. About one-fourth of this solution is permitted to flow out of the capillary by temporarily releasing the clip. Any remaining air which may be entrapped at the lower end of the capillary is displaced by pressing the rubber connection just above the clip several times by hand. The calculated amount of cellulose for producing a solution containing 0.5 percent of cotton or 2 percent of rayon, is introduced into the instrument, which is nearly filled with cuprammonium solution, and the specimen carefully stirred with a fine glass rod to dislodge any entrapped air. The viscometer is completely filled with cuprammonium solution and closed by means of the capillary tube, rubber stopper, flanged rubber tube, and collar, *H*, *J*, *N*, and *L*. In so doing, cuprammonium solution will be forced through the capillary and will partly fill the flanged rubber tube. To insure the displacement of all of the air, the rubber tube is completely filled with solution and then closed with the clip. The parts are kept in place on the ends of the viscometer by rubber bands on the hooks provided for the purpose. The viscometer is then placed on a suitable device, protected from light, and rotated end over end at the rate of about 4 rpm until the specimen is completely dispersed. Rayons, bleached cotton, and degraded celluloses may be completely dispersed in about 4 hours. Cotton celluloses of fluidities less than 3, in a 0.5-percent dispersion, often require a longer time. An effective procedure for such specimens is to rotate them from noon of one day until noon of the next, occasionally stopping the rotation and turning the viscometers about their long axes through an arc of approximately 30° every half hour during the daytime. This is to permit the wedge to slide down the sides of the tubes in different paths and remove the swollen cellulose which tends to adhere to the walls. A device now in use in this laboratory which simultaneously and automatically effects both motions of the viscometer is more convenient and reliable.

After dispersion is complete, the viscometer is immersed in the water in the reservoir (5, fig. 4) and permitted to come to the desired temperature. It is then placed in position, 3, surrounded by water in the jacketed chamber, 2, and the rate of flow determined. The fluidity, η, of the solution is calculated by means of eq 10.

VII. DUPLICABILITY OF FLUIDITY MEASUREMENTS

Dispersions of cellulose that has not been degraded by the action of light, heat, chemicals, or other deteriorative influences have relatively low fluidities, and dispersions of modified celluloses higher fluidities. The first differ most from simple liquids and in consequence the results of fluidity measurements of these are likely to be affected more by differences in viscometers. In order to show the duplicability of the measurements, the fluidities of cotton cellulose in 0.5- and 0.25-percent dispersions and of rayon in 1-percent dispersion were determined. Nine of the viscometers of the group referred to in section V, including the one with the lowest and the one with the highest value for *A* were used. Duplicate measurements were made of the fluidity of the

material in each of the viscometers at 21° C. The results are presented in figure 6.

The average difference in the duplicate results obtained with each viscometer for the 1-percent concentration of rayon is 0.18; for the 0.25-percent cotton, 0.31; and for the 0.5-percent cotton, 0.09 rhes. The average deviations from the mean value for all 18 determinations

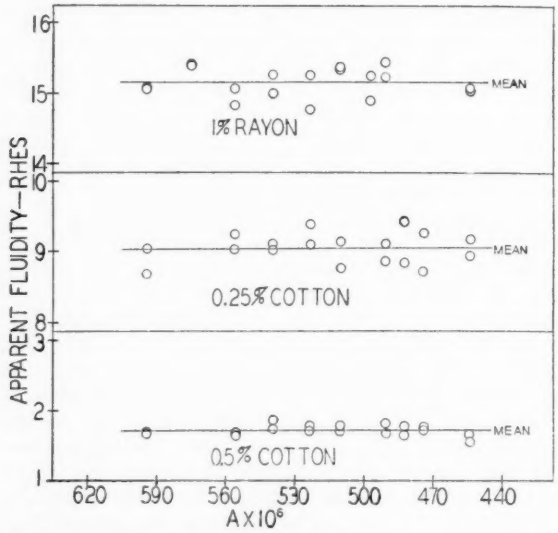

FIGURE 6.—*Data showing the duplicability of results of measurements with the same viscometer, and with viscometers of the same type but differing in their characteristic constant, A.*

The results for two concentrations of cotton dispersions and one of rayon are given. The straight line represents the mean fluidity of each group.

of the fluidity of the rayon, 0.25-percent cotton, and 0.5-percent cotton are 0.17, 0.18, and 0.05 rhes, respectively. It is concluded, therefore, that the viscometers described are sufficiently alike for ordinary purposes.

Acknowledgment is made of the invaluable suggestions of W. H. Herschel on the calibration of viscometers.

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PRINTING TESTS OF EXPERIMENTAL BOOK PAPERS

By Merle B. Shaw and Robert H. Simmons [1]

ABSTRACT

In connection with the previously published study of the "Effect of filling and sizing materials on stability of book papers," RP1149, comparative measurements of printing quality have been made on 45 of the experimental papers. Smoothness, oil penetrability, and air permeability were determined by laboratory tests at the Bureau; the composite effect of all the factors that affect printing, by actual printing trials at the Government Printing Office.

For the same pulp furnish, the smoothness values of the papers were about the same for precipitated calcium carbonate and clay, and less for natural calcium carbonates, titanium dioxide pigments, and zinc sulfide pigments. With respect to their influence on the oil penetrability of the paper, the order in decreasing rapidity of penetration was: Precipitated calcium carbonate, natural calcium carbonate, zinc sulfide pigments, titanium dioxide pigments, and clay. Ranked according to the degree to which they increase air permeability, the order of the fillers was the same as for oil penetration.

The net resultant of all the factors that affect printing is shown by actual printings. In general, the offset printings were of better quality than the letterpress, and the text better than the illustrations. Ratings of the offset printings as to relative amount of "show through" are given. The calcium carbonate-filled papers gave the best results, but it is believed that printing conditions could have been adjusted to suit each type of paper, and that more satisfactory results would then have been obtained with either process.

CONTENTS

	Page
I. Introduction	285
II. Paper samples	286
III. Testing methods	286
1. Laboratory	286
2. Printing	288
IV. Test results	288

I. INTRODUCTION

A study made at the Bureau on the effect of filling and sizing materials on the stability of book papers was recently published.[2] The study was concerned primarily with the characteristics directly related to the stability of paper. Since book papers must fulfill printing requirements, however, the scope of the work has been expanded to include comparison of the papers from the standpoint of printing quality also. The additional data are here reported to supplement the results obtained in the earlier investigation.

[1] Associate Chemist, United States Government Printing Office.
[2] J. Research NBS **21**, 671 (1938) RP1149.

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The manufacture of the experimental papers was described in the previous publication. The fillers used were representative of several types, both natural materials and manufactured pigments. They comprised one clay; two titanium pigments, titanium dioxide, and a composite of titanium dioxide and barium sulfate; two zinc sulfide pigments, zinc sulfide, and a composite of zinc sulfide and barium sulfate; and two calcium carbonates, one precipitated and one a natural product, water-ground. The fibrous materials employed were sulfite pulp and soda pulp of the ordinary book-paper grade; three "purified" wood pulps produced by special cooking and bleaching treatment to obtain high purity and strength; new rags, the grade known commercially as No. 1 white shirt cuttings; and two grades of old rags, No. 1 old whites and "twos and blues."

The test data on the properties which have a considerable influence on the printability of the paper are repeated here. The additional data given consist of laboratory measurements of other characteristics more directly related to the performance of paper in the printing processes and results of observations of actual printings. The laboratory measurements were made at the Bureau; the paper samples were printed at the Government Printing Office.

II. PAPER SAMPLES

Forty-five of the seventy-two experimental papers made in the stability study were selected for the tests of printing quality. They were representative of all the fiber and filler combinations reported in the previous publication.

III. TESTING METHODS

1. LABORATORY

The laboratory tests made for measuring the printing quality of the book papers were smoothness, oil penetrability, and air permeability. Although no methods for determining these qualities have been adopted as standard by the Technical Association of the Pulp and Paper Industry, the methods used in this work are widely employed by Government and by commercial laboratories.

Smoothness is one of the most important properties of paper from the printing standpoint. In letterpress work the printing pressures are high, and part of the ink between the paper and the hard printing block is therefore pressed out, into the recesses between the surface fibers if the paper is rough, or at the edges of the surface of contact if the paper is smooth. Consequently, if there is not uniform contact between the paper surface and the inked printing plate, loss of detail in the reproduction of either solid print or halftones results.

The smoothness of the paper surfaces was measured with a Bekk smoothness tester, and is expressed as the number of seconds required for 10 cm^3 of air at 0.5 atmosphere pressure to pass between 10 cm^2 of the paper surface and an optically flat surface which is held against it by a pressure of 10 kg. The tests were made at 21° C (70° F) and 65-percent relative humidity (standard paper-testing conditions), with the papers tested being in hygrometric equilibrium with the atmosphere of the test room. The values reported are the averages of the measurements on both the felt and the wire sides of the sheets.

Softness of paper also is important in determining printing quality. If the thickness of the paper is somewhat variable, or the letterpress plates slightly irregular, the paper—and in the offset process, the rubber blanket also—should by its compressibility equalize these irregularities. For a given type of paper, with the same smoothness the softer paper will give the better printing results, other things being equal. No measurements of softness were made on the test papers, however, as the value of the present instruments available for the purpose is not yet well known.

The efficiency of the sizing of nonprinting papers is judged by its effectiveness in preventing the spread and penetration of watery liquids, such as writing ink. The effect with printing ink may not be the same. The penetration of printing ink into paper is due primarily to the vehicle used with the pigment. The resistance of paper to "feathering" of writing ink is, therefore, not a measure of the resistance to inks having an oil base. Printing ink consists essentially of a suspension of finely ground pigment in a suitable oil. Since the sizing values reported relate to water penetration, the data are not applicable for comparing the papers from the printing standpoint. To obtain pertinent data the resistance to penetration of printing ink was evaluated with oil instead of water.

The test was made by the "oil drop" method. The time of penetration through the sheet was found by allowing a drop of USP quality castor oil to fall on one side of the paper and measuring the time, in seconds, required for the oil to penetrate the sheet. The end point of the penetration was taken when the spot on the under surface of the paper was uniformly translucent in appearance. The outlet of the delivery tube for the oil was of such size that 25 drops of distilled water at 21° C equalled 1 ml. The values are the averages of the rates of penetration determined from each side of the paper.

The ink used in printing processes dries or hardens by oxidation of the oil vehicle, and by absorption of the oil by the paper. In actual practice, the drying results from a combination of both. In general, the oxidation is a much slower process, and if the paper does not absorb the oil readily, the ink will dry too slowly and it will be prone to "set off" and become smudged on contact with adjacent sheets. On the other hand, if the oil penetrates too rapidly, too much vehicle will leave the image, and a chalky film will result. Also if the oil penetrates too rapidly, the sheet tends to become transparent and the printing may "show through" the opposite side of the paper, especially if a large amount of ink has been required to obtain a solid print. The oil penetration test differs from actual printing by using an excess of oil and allowing it to penetrate completely through the sheet, but the relative penetrability of the papers to printing ink should be of the same order.

Air permeability is not known to be definitely correlated with printing quality, but inasmuch as it relates to the passage of air through paper, it may be of assistance in predicting the permeability of the paper also to liquids, such as oil, that do not materially swell cellulose. Since the test measures the flow of air through the minute passages within the fibers themselves and the spaces between the fibers, it likewise holds possibilities for evaluating and controlling the structure

of the sheet. Keeping the sheet open and bulky is usually considered desirable for optimum printing quality.

The instrument and testing method used for measuring the air permeability were developed at the Bureau and have been described in detail in previous publications.[3] The test consists in measuring the volume of standard air which passes in unit time through a unit area of the material when forced by a unit pressure difference between the surfaces of the sheet. Standard air, for the purposes of this test, is defined as air at 21° C, 65-percent relative humidity, and a pressure of one atmosphere.

2. PRINTING

To afford comparison of the papers for the composite effect of all the factors which affect printability, the papers were submitted to actual printing tests. Since the letterpress and offset processes are the most commonly used with book paper for mass production, they were the only processes considered. The papers were compared with two commercial book papers, described as "machine-finish" and "offset" and used for regular work at the Government Printing Office, in a run made by the procedure regularly employed. The printings were made on one side of the sheet by the letterpress process, in which an inked relief surface is pressed onto the paper, and on the other side by the offset process in which the impression instead of being made directly upon the paper is first received by a rubber blanket, from which it is transferred to the paper. The images printed by both processes consisted of text and halftones.

IV. TEST RESULTS

The smoothness measurements of the test papers are given in the table. The time required for the air to pass over the surface of the paper increases with increasing smoothness of sheet, therefore, a low reading indicates comparatively rough paper; a higher reading, smoother paper. For best printing results the papers should have been more highly calendered, as the machine finish obtained on the small calender stack at the Bureau is possibly not as smooth as commercial machine finish.

Fillers, because of their greater smoothability and smaller particle size, respond more readily than fiber to the pressure of the calender rolls used in the papermaking process to press and smooth the paper, and their presence, therefore, increases the smoothness of the paper surface. Although only a limited number of papers were made and smoothness was not of primary importance in their manufacture, the results indicate a general trend. For the same pulp furnish the smoothness values of the papers were about the same for precipitated calcium carbonate and for clay, and less for natural calcium carbonates, titanium dioxide pigments, and zinc sulfide pigments. Although the manufacturers of the titanium dioxide and the zinc sulfide pigments state that only small proportions are generally used in paper, since the study for which the papers were made was concerned mainly with the effect of the pigments on stability, 5 and 15 percent were each used in the experimental runs. The amount of clay added was

[3] BS J. Research **12**, 567 (1934) RP681; BS J. Research **12**, 587 (1934) RP682.

15 percent; of calcium carbonate, 15 or 30 percent. The test results should be regarded as applying only to the materials used, which were representative at the time the work was done. The relationship may be changed with further improvement in quality of the materials with further advance in manufacturing technique.

For the same filler furnish, the old-rag papers were the highest in smoothness; the sulfite-soda, new rag, and purified wood pulps *A* and *C* (mixture) papers were intermediate; and the purified wood pulp *D* was lowest. Comparison of the tests with the printings indicates that the papers having the higher smoothness values gave the better letterpress printing results. The offset process is less exacting than the letterpress with respect to smoothness.

TABLE 1.—*Test data on the experimental book papers*

Paper machine run number	Fiber used	Filler used	Tests of papers [2]											Rating of "show through"—offset printings [5]
			Weight: 25 by 40 inches, 500 sheets	Thickness	Filler [1]	Resin [1]	Acidity [3] (glass electrode method)	Degree of sizing (dry indicator method)	Opacity (contrast ratio)	Smoothness [4] (Bekk instrument)	Oil penetration [4]	Air permeability		
			Pounds	*Inch*	*Percent*	*Percent*	pH	*Seconds*	*Percent*	*Seconds*	*Seconds*	*cm³/sec/m³/g/cm³*		
1133	Sulfite pulp, 50%; soda pulp, 50%.	None	57.6	0.0035	------	0.3	6.9	------	81	35	158	50.6		47
1143	do	do	55.9	.0037	------	.9	5.8	49	83	40	145	62.0		46
1130	do	Clay	55.5	.0035	10.1	.2	5.3	------	87	68	103	94.0		45
1137	do	do	55.6	.0037	10.6	1.6	5.5	40	88	65	112	98.0		37
1140	do	do	56.1	.0036	10.0	1.0	5.9	42	88	68	111	81.5		38
1141	do	do	57.6	.0037	11.8	1.2	5.2	47	89	58	105	96.0		21
1142	do	do	55.7	.0036	12.6	1.0	6.5	48	89	67	110	91.7		22
1147	do	Titanium pigment *A*	54.9	.0035	9.0	1.0	5.2	38	94	48	108	85.9		4
1145	do	do	57.1	.0037	3.1	.9	5.6	59	90	36	118	65.9		23
1149	do	Titanium pigment *B*	56.5	.0035	[6]3.2; 6.6	1.1	5.2	45	92	46	96	98.2		28
1150	do	Zinc sulfide pigment *A*	56.0	.0035	9.4	1.1	5.8	44	94	44	104	84.5		2
1151	do	do	55.1	.0034	2.3	.9	5.7	59	88	39	110	71.3		44
1153	do	Zinc sulfide pigment *B*	55.0	.0033	[7]6.2; 5.1	1.2	5.1	47	94	48	78	121.4		3
1158	do	Prec. calcium carbonate	56.0	.0037	7.2	.5	9.6	0	90	49	96	101.1		29
1172	do	do	56.9	.0039	11.2	1.6	8.9	13	92	67	90	118.3		7
1173	do	do	55.9	.0037	21.1	1.6	8.8	6	93	116	69	128.3		6
1174	do	Natural calcium carbonate *A*	56.7	.0037	16.4	.3	9.2	0	86	56	70	131.9		42
1175	do	do	56.4	.0037	9.9	1.3	8.5	23	87	51	103	104.9		43
1220	do	Natural calcium carbonate *C*	55.4	.0034	21.2	1.1	8.8	11	93	99	80	92.5		8
1161	Purified wood pulp: *A*, 75%; *C*, 25%.	Clay	55.0	.0034	11.5	1.6	6.1	24	88	59	109	62.7		25
1162	do	do	57.4	.0036	11.9	1.7	5.6	31	87	63	114	65.8		26
1164	do	do	56.5	.0033	12.1	1.1	6.0	13	87	63	118	60.6		27
1165	do	do	58.1	.0036	11.9	1.1	5.6	22	88	52	116	65.6		24
1168	Purified wood pulp: *D*, 100%	do	55.1	.0033	13.5	.9	6.4	14	83	28	[8]300	9.5		40
1169	do	do	56.9	.0036	13.9	.9	5.8	17	84	28	[8]300	11.3		41

1177	Rags: No. 1 new whites, 100%.	do	55.9	.0035	14.0	.3	6.4	0	88	51	130	33.8	31
1180	do	do	56.1	.0034	13.6	1.8	5.6	9	89	64	146	30.2	32
1181	do	do	54.9	.0033	13.0	1.7	5.4	7	89	64	148	32.4	33
1184	do	do	55.0	.0035	13.6	.9	5.6	3	88	54	145	28.4	34
1185	do	do	56.0	.0035	12.7	.9	5.1	5	88	56	144	31.8	35
1192	Rags: No. 1 old whites, 50%; twos and blues, 50%.	do	57.1	.0038	13.8	.2	5.8	1	91	64	76	89.9	16
1201	do	do	56.5	.0035	13.7	1.4	5.9	6	92	65	87	66.4	17
1202	do	do	54.8	.0037	13.7	1.5	5.5	5	91	62	80	77.0	18
1214	do	None	55.1	.0038		.5	6.2	3	86	32	112	60.4	39
1204	do	Clay	56.9	.0039	13.4	.5	6.2	3	91	72	92	73.7	13
1205	do	do	55.9	.0038	14.0	.5	5.4	3	91	82	85	70.2	10
1207	do	Titanium pigment *A*	57.4	.0038	4.6	.8	5.2	6	92	49	87	76.3	11
1209	do	Titanium pigment *B*	57.1	.0037	[6]4.2; 8.4	.8	5.6	5	93	73	67	98.6	12
1210	do	Zinc sulfide pigment *A*	56.4	.0039	4.3	.8	6.1	5	94	34	74	101.5	19
1212	do	Zinc sulfide pigment *B*	57.4	.0037	[7]6.9; 5.6	.9	5.5	3	95	46	64	99.4	5
1215	do	Prec. calcium carbonate	55.2	.0036	14.0	.1	9.5		91	75	52	113.4	14
1216	do	do	55.3	.0033	28.2	.1	9.5		93	138	32	140.0	1
1217	do	Natural calcium carbonate *C*	56.4	.0037	11.8	.1	9.4		90	52	68	84.0	15
1218	do	Natural calcium carbonate *B*	55.6	.0037	12.4	.2	9.4		89	68	67	99.1	36
1219	do	Natural calcium carbonate *A*	55.9	.0037	12.2	.2	9.4		89	67	63	105.1	30
Commercial machine-finish book (Government Printing Office)			53.0	0.0033					91	90	56	183.3	20
Commercial offset book (Government Printing Office)			64.0	.0041					91	68	132	144.3	9

[1] On oven-dry basis.
[2] Cold water extraction, unpublished method.
[3] Tests made at 65-percent relative humidity and 70° F.
[4] Averages of measurements on both felt and wire sides of sheets.
[5] Relative amounts, in increasing order.
[6] Titanium dioxide and barium sulfate, respectively.
[7] Zinc sulfide and barium sulfate, respectively.
[8] End point had not been reached at end of 5 minutes.

The papers containing fillers were penetrated by oil more rapidly than the papers without fillers. Fillers increase the specific surface of the absorptive constituents of paper. The wetting properties of the fillers and the cellulose materials used, as well as the number and size of the minute channels within the sheet also doubtless influence the rate of oil penetration. The order of the wettability of either fillers or fibers may differ in the cellulose-filler combination of paper, however, from that of the individual materials. With respect to their influence on the oil penetrability of the paper, the test data show the order of the fillers, in decreasing rapidity of penetration, to be: Precipitated calcium carbonate, natural calcium carbonate, zinc sulfide pigments, titanium dioxide pigments, and clay. The order of the pulps is: Old rags, sulfite-soda mixture, purified wood pulps *A* and *C* (mixture), new rags, and purified wood pulp *D*. There is no apparent correlation between degree of sizing and rate of oil penetration.

In the test of the papers containing titanium dioxide pigment the oil seemed to take considerable time to penetrate the upper surface of the sheet and also to form a uniformly gray end point just before penetrating the lower surface of the sheet. This skin effect may indicate a higher resistance of the pigment to wetting and permit obtaining comparable printing results with a lower content of filler than is possible with other kinds of fillers.

The sharpness of the end point for the oil-drop penetration, regardless of the type of filler present, was most pronounced for the sulfite-soda papers, with the old rag, purified wood pulps *A* and *C* (mixture), new rag, and purified wood pulp *D* papers following in the order given.

The air permeability was greater for the papers containing fillers than for those without fillers. By inclusion of fillers the tendency of the fibers to cement together is lessened. The number of internal air spaces, and consequently the air permeability of the paper, are therefore increased. Ranked according to the degree to which they increase air permeability, the fillers are in the following descending order: Precipitated calcium carbonate, natural calcium carbonate, zinc sulfide pigment, titanium dioxide pigment, and clay, although only slight differences are shown for the last three. The corresponding order for the pulps is: Sulfite-soda, old rag, purified wood pulps *A* and *C* (mixture), new rag, and purified wood pulp *D*. The measurements for the individual sheets of the sample were in very good agreement.

There appears to be a definite relationship between the air-permeability and the oil-penetration data, the more open sheet having the more rapid oil penetration, but too few measurements on the same type of paper were made to warrant a numerical correlation.

The net resultant of all the factors that affect printing is shown by actual printings. In general, the offset printings were of better quality than the letterpress, and the text better than the illustrations. The ink and the mechanical phases of the printing process are ordinarily adjusted for each specific paper to be printed, but the experimental papers were all printed with the same ink and the same press adjustments—those used for the commercial papers with which the test sheets were run. The basis weight and thickness were practically uniform for all the papers, but there was considerable variation in their fiber and filler composition, which would be expected to cause the papers to have different wetting or absorptive properties. Better

ratings are therefore given for the offset printings because smaller, and more nearly uniform, amounts of ink were used. It is believed that printing conditions could have been adjusted to suit each type of paper, and that more satisfactory results would then have been obtained with either process.

The appearance of the text was satisfactory for all the offset printings. With some of the papers there was "show through" of the cuts, that is, print was visible on the opposite side of the sheet. The table gives ratings of the offset printings as to relative amount of "show through," in increasing order. The ratings were determined by visual observation. Although each of the printings is assigned a specific position in the series, several could be grouped as of practically the same quality.

The paper of machine run 1216 was rated as freest from "show through." This paper was made from a pulp furnish of old rags with a relatively high percentage of calcium carbonate. Next in rank were the papers of runs 1150 and 1153. These, and the remaining samples containing zinc sulfide pigments were considerably darker in color [4] than the other papers, however, and their rating on "show through" might not have been the same if they had been lighter-colored. The rating of the samples containing titanium dioxide pigments was in agreement with the behavior noted in the oil-penetration test. Since the initial rate of penetration is slow, the ink must be carefully controlled to prevent "set off" and smudging, but there should be little "show through."

For letterpress printing the calcium carbonate-filled papers gave the best results. As to "show through" the letterpress printings were in approximately the same order as the offset. Disagreements were in general attributed more to variations in the amount of ink on the images than to the paper.

The papers made from the mixture of purified wood pulps *A* and *C* were about the same as the sulfite-soda and the old-rag, all being satisfactory. A tendency of the ink to "lift" or "pick" was noted for the harder papers, but as the ink was adjusted to comparatively soft paper, it doubtless was not strong, or tacky, enough for these sheets. The papers made from purified wood pulp *D* were too hard for book paper, as noted in the previous publication,[5] because of too rapid hydration of the pulp during the beating. The new-rag papers were only fair, also doubtless because of the method of stock preparation. Quicker beating would have produced softer paper, with greater air permeability and more rapid oil penetration, and as a result, improved printability.

The color of the paper influenced the evaluation of clearness of print—letterpress or offset—to some extent, the whiter samples ranking higher than the natural colored. For some of the papers the difference in color was caused by differences in the pulps used, but for those having the same pulp furnish the difference was due to the fillers. No dye was used for tinting any of the papers.

[4] As explained in RP1149, the darker color of these papers was attributed to the copper lining of the beater and the acidic condition of the pulp during the preparation of the stock. As a precautionary measure the supplier of the zinc sulfide pigments recommends that plants having considerable copper equipment "avoid acid conditions so excessive as to attack this equipment and to form a dilute copper solution, as such a condition can dull down the white pigment to an extent dependent upon the amount of copper in solution and the time available for the reaction." Since the program of study included the manufacture at pH 4.2 of some papers with each filler, dulling of the papers pigmented with zinc sulfide was expected.

[5] J. Research NBS **21**, 671 (1938) RP1149.

Printing trials are the ultimate criteria for evaluating the printing quality of paper, but laboratory tests should enable the manufacturer to ascertain before shipment of his paper that it will have the requisite printing properties. Opacity and smoothness are known to be related to printing quality and therefore have a place in paper specifications. Less is known of the relation of oil penetration and air permeability, but it is believed that they also are indicative of the behavior of paper in actual printing. As data on these tests are accumulated for different types of filler and pulp furnishes and correlated with the quality of printing, it may be found that numerical specifications of these additional properties can be included to aid in controlling printing quality within predetermined limits.

The authors acknowledge their indebtedness to the following members of the Bureau: R. W. Carr, M. J. O'Leary, and V. Worthington for assistance in the preparation and testing of the papers, and to M. N. V. Geib and C. G. Weber for rating the printings.

WASHINGTON, January 4, 1939.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1181

Part of Journal of Research of the National Bureau of Standards, Volume 22, March 1939

A PRECISION RADIO INSTRUMENT FOR TRANSMITTING MEASUREMENTS OF ULTRAVIOLET INTENSITIES FROM UNMANNED BALLOONS TO A GROUND STATION

By R. Stair

ABSTRACT

A new radio stratosphere ultraviolet meter which operates with a precision comparable to that of laboratory instruments is described. It consists of a photoelectric cell, a balanced amplifier, a relaxation oscillator, and a transmitter. The calibration of the instrument is automatically determined and broadcast to the receiving station each time an altitude signal is given. The instrument, with accessories, including sufficient batteries to operate for about 4 hours, weighs about 5 pounds. It operates on a frequency of approximately 50 megacycles and has sufficient power to insure good reception for distances from the receiving station up to 100 miles.

The present instrument was developed subsequent to the making of six flights into the stratosphere with a three-tube unit during the summer of 1937 [1],[1] although a laboratory model was tested and briefly mentioned in the report covering that work.

Because of the very high photoelectric cell and grid resistances involved, the three-tube instrument was difficult to either operate or calibrate; in that it was subject to instability as the result of the relaxation oscillator being worked beyond its stable range. Furthermore, changes in sensitivity and proportionality of response, as the battery voltages dropped, offered insurmountable difficulties in the use of that instrument.

The present instrument, shown diagrammatically in figure 1, virtually combines the balanced direct-current amplifier [2] previously designed for precision work in the laboratory with a relaxation oscillator and short-wave transmitter [3] similar to that developed by Diamond and his collaborators. Sufficient power and sensitivity are available in the new instrument for the relaxation oscillator to operate under normal conditions of circuit and voltage and hence in a condition of stable equilibrium.

Briefly described, the balanced direct-current amplifier, built in the form of a Wheatstone bridge, becomes unbalanced when light falls upon the photoelectric cell. Here the effect produced in the plate circuit, which is also the grid circuit of the relaxation oscillator tube *1A6*, may be made several hundred times that possible when using the photoelectric cell coupled directly to the relaxation oscillator, as in the earlier instrument. Thus, in the new instrument, the resistance in the grid circuit of this tube is reduced from hundreds to a few megohms (to 2.6 megohms in the instrument as described). With a

[1] Figures in brackets indicate the literature references at the end of this paper.

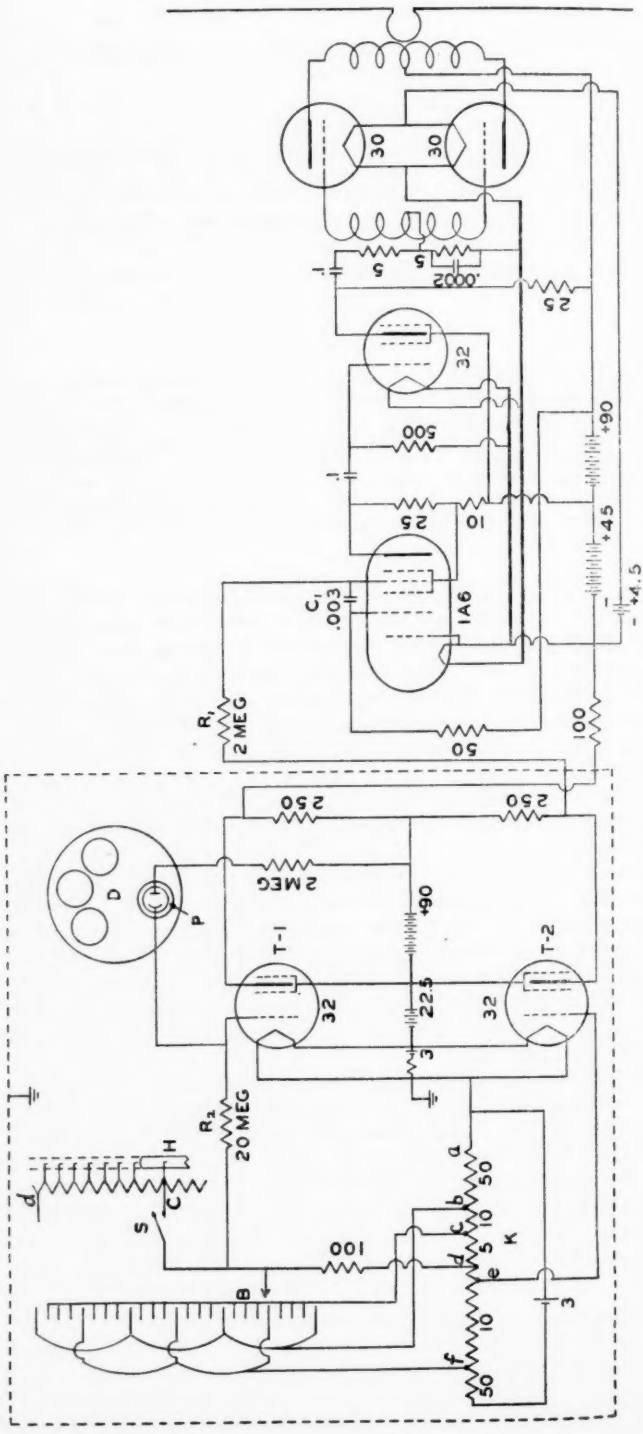

FIGURE 1.—*Electrical circuit of the new stratosphere ultraviolet meter.*

Resistances are given in thousands of ohms and capacitances in microfarads, except where definitely specified otherwise.

grid resistor of this magnitude, the relaxation oscillator operates normally and thus repeats consistently from day to day.

The capacitance, C_1, and the resistance, R_1, plus the additional resistors between C_1 and grid 1 of the relaxation oscillator tube *1A6*, determine the sensitivity and the base value (oscillation frequency with no light on the photoelectric cell) of the relaxation oscillation. Values of 0.003 μf and 2.6 megohms, respectively, used in this instrument, give a base frequency of about 50 cycles and provide the correct sensitivity for coupling with the balanced amplifier as used here, when the other constants of the *1A6* tube circuit are as given in figure 1.

The generated audio-frequency voltage is next amplified and finally modulates a push-pull radio-frequency oscillator coupled to a half-wave doublet antenna. The grid and plate coils are closely coupled, being alternately wound with No. 16 enameled copper wire on a ⅞-in. Pyrex tube.

Each coil consists of six turns of wire, center tapped. The antenna coupling coil consists of one turn of wire near the center of the oscillator coils. The antenna is adjusted for maximum power output of the oscillator which operates at approximately 50 Mc (6 m). Tests have shown that the transmitter has sufficient power to insure static-free reception and hence a good record up to a distance of 100 miles from the recording station.

Having the relaxation oscillator and transmitter properly operating, the direct-current amplifier is next adjusted. The two type 32 tubes must be closely similar in characteristics or they will not work satisfactorily in this circuit.

The bias on tube *T–2*, is adjusted to approximately −1.5 v (point, *e*, on the potentiometer, *K*). Next, the connection, *d*, is adjusted to give the proper bias on tube, *T–1*, so that but little change is observed in the relaxation oscillation frequency when the amplifier is turned on; a slight increase in frequency is to be preferred to that of a decrease.

The value of the grid resistor, R_2, is so chosen as to give the proper sensitivity required of the amplifier for use with the particular photoelectric cell, *P*, employed in the unit. A change in R_2 ordinarily calls for a change in the bias of *T–1*, since the accompanying grid-current change is sufficient to unbalance the amplifier and hence modify the relaxation oscillation frequency.

In operation, as a small motor [1] rotates the disk, *D*, carrying various filters over the photoelectric cell, the amplifier becomes unbalanced in a degree proportional to the intensity of light reaching the cell. This unbalance in the plate circuit of the amplifier gives rise to a new voltage difference in the grid circuit of the *1A6* relaxation oscillator tube. This voltage change causes in turn an increase in the control grid current in the tube, thus increasing the charging rate of condenser, C_1, and hence the frequency of oscillation. Tests using perforated screens of known transmission in the path of light show a closely linear change in audio-frequency oscillation with light intensity. The several instruments built and tested gave frequency changes which were linear to within about 1 percent throughout the range of 50 to 200 c/s, for which they were designed. Figure 2 shows a record when three perforated screens having transmissions of 12.9, 48.1, and 91 percent were being used to test the performance of the instrument. As a further precaution, in practice, each optical filter is used with an

accompanying perforated screen having approximately the same transmission so that any possible deviations from linearity in either the radiometeorograph or the ground-station receiver and recorder are automatically compensated. This is very important since the calculations on the spectral quality of the ultraviolet radiation and the amount of ozone penetrated are based upon the absolute value of, and changes in, the filter transmissions as the instrument reaches higher altitudes.

The barograph, *B*, not only indicates the altitude as the arm makes contact with a selected segment, *b*, *c*, or *f*, but impresses a definite voltage, for example, that across *cd*, on the grid of tube, *T–1*, which in turn causes an increase in audio-frequency oscillation indicative of the absolute sensitivity of the complete instrument. This is illustrated by the change in frequency of the base line from *d* to *c* in figure 2. When a contact is made with a segment connected to *b* the base

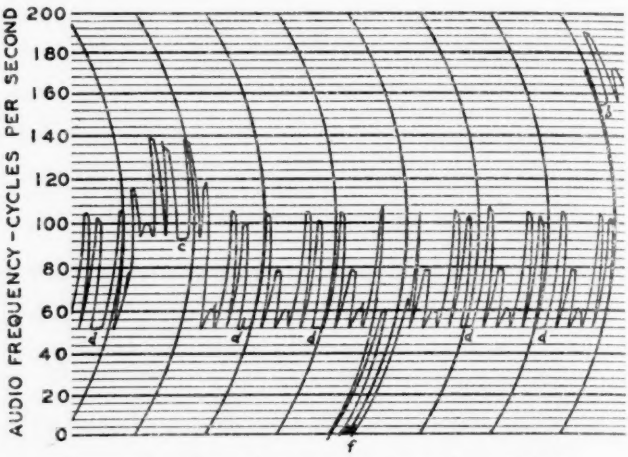

FIGURE 2.—*Chart showing type of record transmitted.*

frequency is raised still higher. On the other hand, when a contact is made to *f* the base frequency is lowered, and may be made zero. In practice, the contacts *b* and *f* are used as reference points of altitude only, while the more numerous contacts, *c*, are used both for sensitivity calibration and altitude determination.

A projected modification of the barograph is the addition of a small auxiliary mercury U-tube unit to give an absolute indication of pressure, and hence, altitude for elevations above 60,000 ft (18 km). This modification will also give an automatic sensitivity test for each cycle of measurements, since the switch, *S*, is to be closed once during each rotation by a cam on the filter disk shaft. This unit is to be placed in the potentiometer circuit, *K*, between *c* and *d*. (See upper part of fig. 1.) That is, the resistor, *cd*, is to be broken, say into 1,000-ohm, steps, each being connected to an electrode in the small mercury U-tube, so that as the pressure decreases and the mercury rises in the open end of the tube, successive sections of the resistor are short-circuited, resulting in decreased audio-frequency changes upon the closing of switch, *S*. These changes will be easily recognizable on the record.

As shown in figure 1, the direct-current amplifier, barograph, *B*, photoelectric cell, *P*, and all connecting leads are completely shielded with aluminum foil which is grounded to the negative of the filament battery. This is necessary in order to eliminate electrostatic effects which would otherwise be uncontrollable in the calibration and use of the instrument.

The relaxation oscillator and transmitter require a separate set of filament and plate batteries since they operate at a potential which constantly varies relative to that of the amplifier. Furthermore, it is necessary that the two units be carefully insulated or variable leakages will produce inconstancy in the base of the audio-frequency signal. For this purpose the transmitter is mounted on Bakelite and the transmitter batteries are wrapped in thin rubber.

The aim has been to make the various units of this instrument small and light in weight and yet retain materials of sufficiently good quality to insure precision operation. All tube bases are removed and the wires soldered directly to the protruding electrodes. The batteries have been chosen of minimum size sufficient to give about 3 to 4 hours of dependable operation at the reduced temperatures encountered. For the filament current in the balanced amplifier, two standard flashlight cells in series are used to operate the two type 32 tubes in parallel. The four tubes in the relaxation oscillator transmitter unit are wired in series parallel, so that three standard flashlight cells in series give the same useful life as the two in the amplifier. Batteries of the Burgess types *V30FL* and *W30FL* are employed for the plate voltages in the amplifier and transmitter, respectively.

For the potentiometer, *K*, two type *Z* Penlite cells in series are permanently shunted by approximately 120,000 ohms. After a few days, they reach an equilibrium value which changes but little over a period of weeks. Upon the constancy of these cells and resistors depends the calibration of the radiometeorograph from the time it is tested in the laboratory until the flight is finished.

For lightness and compactness most of the resistor units are of the standard 0.5-watt type. In the grid and plate circuits of the balanced amplifier, however, S. S. White or wire-wound units are used to give more reliable and stable operation of the amplifier. This precaution is very important since a small change in this part of the circuit, for example, a defective resistor in the plate circuit of one of the amplifier tubes, may, through fluctuation in magnitude, shift the audio-frequency base level (*d*, in fig. 2) off the scale in either the positive or negative direction. A slight drift, usually downward, generally occurs as the battery voltages decrease. This is not a serious matter, however, as long as the drift is not sufficient to reach the nonlinear portion of the scale toward the lower frequencies, because the absolute sensitivity of the complete instrument (amplifier and relaxation oscillator) is checked each time a barograph contact is made.

The complete instrument (weighing about 5 lb.) compactly inclosed in a small balsa-wood box (6 by 6 by 9 in.) is wrapped in cotton and black cloth to prevent the batteries from chilling at the low temperatures prevailing in the stratosphere. The box is supported at the four corners by linen threads adjusted to keep the photoelectric cell horizontal, and attached to the upper half of the antenna which in

turn is used for supporting the instrument and incidentally kept taut. The lower half of the antenna is kept stretched by a small weight attached to the lower end. Thus the radio frequency is held fairly constant and fading because of frequency shift is minimized.

Details on the characteristics of the cadmium-alloy photoelectric cell, the optical filters used, and a discussion of the method of evaluating the data for determining the intensity of the ultraviolet radiation and the distribution of ozone in the stratosphere have been outlined in the report on the 1937 flights [1]. Data obtained in the six flights with this instrument during June 1938 are being assembled and will be published in the Journal of Research of the National Bureau of Standards [4].

Although the instrument as described here was designed for use in the study of ultraviolet intensities and ozone distribution in the stratosphere while being transported by small unmanned balloons, its usefulness may be extended to other fields. The method of coupling a receiver of low sensitivity (the photoelectric cell) with a relaxation oscillator offers a practical means for recording directly, or for transmitting to a remote station before recording, any data obtainable in the form of variation in radiation intensity. For a stationary instrument a more elaborate unit with greater flexibility of adjustment and control would be desired. In case the radio transmitter is omitted, the audio-frequency signal from the relaxation oscillator, after proper amplification, would be impressed directly upon the grid circuit of the frequency meter in the recording system.

[1] R. Stair and W. W. Coblentz, J. Research NBS **20,** 185 (1938) RP1075.
[2] W. W. Coblentz and R. Stair, J. Research NBS **12,** 231 (1934) RP647.
[3] H. Diamond, W. S. Hinman, Jr., and F. W. Dunmore, J. Research NBS **20,** 369 (1938) RP1082.
[4] W. W. Coblentz and R. Stair, J. Research NBS **22** (May 1939).

WASHINGTON, December 20, 1938.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1182

Part of Journal of Research of the National Bureau of Standards, Volume 22, March 1939

PREPARATION OF OXYGEN OF HIGH PURITY

By Martin Shepherd, E. R. Weaver, and S. F. Pickering

ABSTRACT

Oxygen, which contained no significant amounts of lower- or higher-boiling impurities, was prepared by a method whose essential feature was the elimination of nitrogen. This oxygen is one of several reference samples being used in connection with the maintenance of the International Temperature Scale at the National Bureau of Standards.

CONTENTS

	Page
I. Essential feature of the method	301
II. Apparatus	302
III. Procedure	303
1. Removal of dissolved gases from the electrolyte	303
2. Removal of adsorbed and occluded gases from the platinum catalyst	303
3. Purification and collection of the oxygen	304
IV. Purity of the oxygen	304
V. Significance of the impurities	305
VI. Final treatment and transfer of oxygen to the saturation pressure thermometer	306

I. ESSENTIAL FEATURE OF THE METHOD

Oxygen of high purity has been prepared by various chemical and physical methods. A complete bibliography of the subject would exceed the length of this paper.[1] Two important facts to be derived from a study of the literature are: (1) the methods of preparation did not exclude the possibility of traces of nitrogen as an impurity, and (2) the methods of purification may have introduced additional traces of nitrogen. Distillation, sometimes resorted to for the final purification, probably failed to remove the last traces of nitrogen.

These facts become apparent when the methods of preparation and purification are considered. Some nitrogen may be expected in oxygen prepared from the electrolysis, thermal dissociation, or reaction of solid or liquid reagents containing dissolved or occluded nitrogen. Subsequently, oxygen purified by passage through solid or liquid reagents will become contaminated with nitrogen dissolved or occluded in these reagents. The complete removal of nitrogen from such reagents, prior to the preparation and purification of oxygen, requires more exacting procedures than have been employed previously.

[1] For representative work of the most exacting nature, the following references are given: Morley, Smithsonian Contributions to Knowledge (1895); Germann, J. Phys. Chem. **19,** 437 (1915); Moles and Gonzales, J. chim. phys. **19,** 310 (1921); and Baxter and Starkweather, Proc. Nat. Acad. Sci. U. S. **10,** 481 (1924).

Finally, in oxygen separated from air, nitrogen (and argon) are the predominant impurities to be expected. Distillation in the laboratory can scarcely be expected to remove these impurities completely.[2] Similarly, distillation cannot be trusted to remove the last traces of nitrogen from oxygen prepared chemically.

The essential feature of the method herein described is the critical removal of nitrogen from both reagents and apparatus prior to the actual generation and purification of the oxygen. With this primary consideration in mind, the electrolysis of an aqueous solution of barium hydroxide was selected as the most suitable means of producing oxygen. There are good reasons for this choice. Dissolved gases may be completely removed from the electrolyte before the oxygen is prepared. Thereafter, no impurities are introduced which cannot be removed by combustion over heated platinum and subsequent condensation to negligible vapor pressures. Occluded gases can be removed from the platinum catalyst before the combustion. Necessary reagents are reduced to a minimum, and no extensive purification "train" is involved. Solid reagents, which are most apt to introduce nitrogen, are avoided with the single exception of platinum.

II. APPARATUS

The photograph of the apparatus is lettered in alphabetical sequence for the reader's convenience. The various parts are:

A, vacuum-type needle valve with fine-pitch adjustment for controlling the pressure in the electrolytic generator.

B, barometric mercury seal serving as a manometer and pressure relief.

C, condenser.

D, electrolytic cell. The platinum electrodes are sealed through glass tubes entering at the top. These tubes are filled with mercury to provide contact with the source of power. Glass-wool filters at the exits prevent the entrainment of spray.

E, condenser.

F, barometric mercury seal.

G, combustion tube. This is made of Pyrex glass, and is a water-jacketed tube of 5-mm bore which contains a platinum spiral 300 mm in length. It is provided with a small condenser at the outlet. Such tubes have been described by Weaver and Ledig.[3]

H, condenser with glass-wool filter.

I, McLeod gage for measuring vacuum.

J, condenser and distillation tube with glass-wool filter.

K, graduated capillary for measuring small amounts of liquid oxygen.

L, saturation pressure thermometer to be filled with oxygen.

M, condenser.

N, differential manometer used in measuring the purity of the oxygen.

O, barometric mercury seal.

P, two-stage mercury-vapor pump (backed by a Hyvac pump, not shown).

X, a bypass, not shown in the photograph, is sealed to the two horizontal exit tubes of the generator, *D*. This bypass consists of an inverted U connection with a stopcock.

The stopcocks of the apparatus are conveniently numbered. They are one-way, oblique-bored cocks of the hollow-blown type, with especial grinding suitable for vacuum work.

The apparatus is fused together as a single unit. (The four rubber tubes shown in the photograph carry cooling water to and from the jackets of the combustion tube and pump.) The portion to the left

[2] Exhaustive fractional rectification of large amounts of oxygen might possibly accomplish this desideratum, but the literature affords no evidence of efforts which were sufficiently heroic.

[3] E. R. Weaver and P. G. Ledig, J. Ind. Eng. Chem. **12**, 368 (1920).

Research Paper 1182

Journal of Research of the National Bureau of Standards

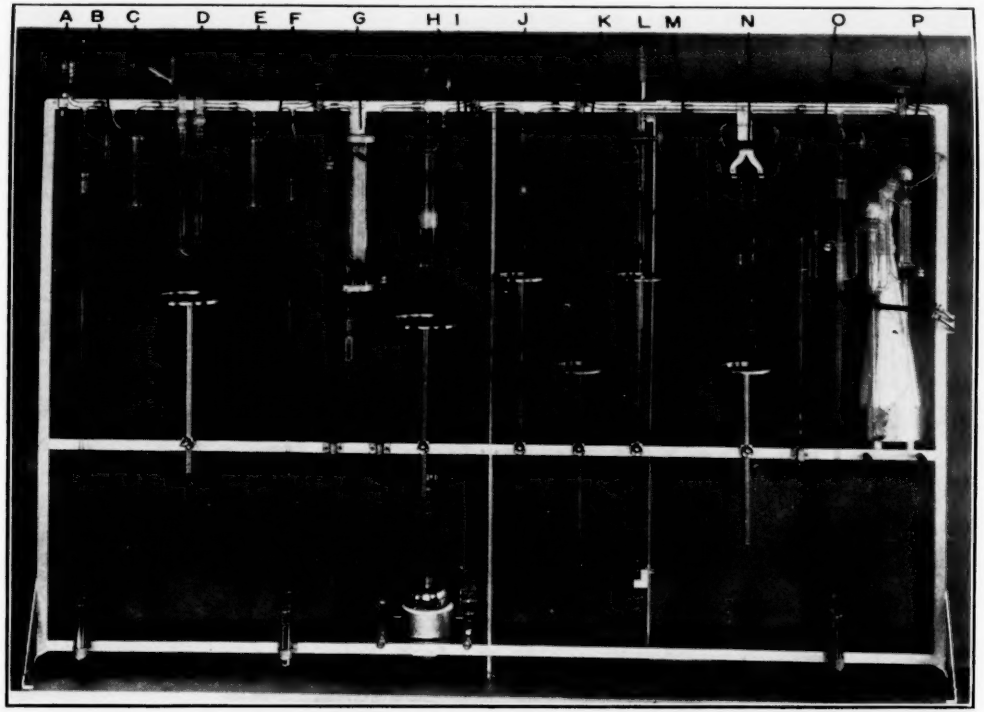

FIGURE 1.—*Apparatus for preparing oxygen of high purity.*

of the combustion tube is blown from a soda-lime glass, and the rest is made of Pyrex glass. A graded glass seal serves to join the two sections.

III. PROCEDURE

1. REMOVAL OF DISSOLVED GASES FROM THE ELECTROLYTE

Barium hydroxide of reagent quality was dissolved in distilled water, and the filtered solution was transferred to the electrolytic cell through the top inlet, which was then fused shut. The solution was frozen within the cell, the entire apparatus was evacuated, and the condensers, *C* and *E*, were immersed in liquid air. Ice from the cell was slowly sublimed into these condensers while the pump, *P*, was continuously withdrawing the liberated gases. Nearly all of the water was removed in this manner. The procedure was reversed to return the ice from *C* and *E* to the cell. This process of vacuum sublimation is known to be effective for removing gases from liquids.[4]

Following the vacuum sublimation of the electrolyte, oxygen and hydrogen were generated slowly over a period of about 100 hours. During this time, the bypass, *X*, was opened and stopcock 1 closed. The gases were withdrawn by a vacuum pump connected to the valve, *A*. A pressure slightly higher than the vapor pressure of the solution itself was maintained. Under this condition, the gases were evolved in such minute bubbles that the solution appeared milky. The bypass, *X*, was closed occasionally, and the solution in the cell was allowed to flow partially from one arm of the U to the other, thus mixing the portion which lay below the electrodes. This whole procedure seems well suited to remove all dissolved gases except oxygen and hydrogen.

Thus two independent methods were used to critically remove dissolved gases from the solution of barium hydroxide.

2. REMOVAL OF ADSORBED AND OCCLUDED GASES FROM THE PLATINUM CATALYST

While the second of the two operations just described was being conducted, the platinum wire within the combustion tube was heated electrically to "whiteness," a temperature considerably in excess of that used subsequently for the combustion of hydrogen. The pump was connected to the combustion tube and to the entire right-hand section of the apparatus. When the pressure measured by the McLeod gage was reduced to 0.0001 mm Hg, the pump was disconnected by closing stopcock 9. The pressure was observed to increase, which indicated that the hot platinum and glass reluctantly gave up the adsorbed and occluded gases. Evacuation was then resumed. When finally the pressure remained lower than 0.0001 mm for a period of 6 hours with the pump disconnected, the platinum was considered suitable for use as a catalyst. (The generation of the oxygen later collected required 6 hours.) This desired condition was achieved after about 120 hours of evacuation.

By the same criterion, the apparatus itself was judged to be sufficiently freed from adsorbed gases.

[4] One account of the process is given by J. H. Hibben, BS J. Research **3**, 97 (1929) RP87.

3. PURIFICATION AND COLLECTION OF THE OXYGEN

The by-pass, *X*, was now closed, and the valve, *A*, was adjusted so that the solution remained level in the two arms of the electrolytic cell. Since twice as much hydrogen as oxygen is generated and the cell itself is a sensitive manometer, the manipulation of the valve required considerable skill. The pressure in the cell was increased until hydrogen and oxygen bubbled through the seals, *B* and *F*. Cocks 2 to 10, inclusive, were closed. The condenser, *H*, was immersed in a bath of liquid oxygen. The temperature of the platinum wire was lowered from "white" to a "cherry red." Stopcock 1 was then opened *very* slowly, and the pressure was slowly increased in *G* and *H* to approximately 740 mm. At this pressure and at the temperature of the bath of oxygen, the oxygen within the condenser did not liquefy. On the other hand, any higher-boiling impurities which might conceivably be present after the combustion were condensed to negligible vapor pressures. Any small frozen particles were retained on the glass-wool filter and thus could not escape to reappear upon vaporization in the effluent gas.

Following these operations, cocks 3, 4, and 9 were opened *very* slowly and in succession, and pressure was allowed to build up in each part of the apparatus so opened. Oxygen was then discarded through cock 10 until the apparatus was thoroughly purged. This precaution was observed because of unavoidable though very slight surges of pressure which occurred through the combustion tube during the period of adjustment of pressure throughout the apparatus.

The condenser, *J*, was now immersed in freshly liquefied air, and about 20 ml of oxygen was condensed therein as fast as it was generated in *D* and purified in *G* and *H*. Thereafter, stopcock 3 was closed.

IV. PURITY OF THE OXYGEN

The purity of the oxygen was measured by a sensitive method based on the observation of differential saturation pressures.[5] The oxygen collected in the tube, *J*, was separated into three fractions by isothermal fractional distillation at −200° C. These fractions were: A very small amount of initial distillate; a middle fraction which was condensed in *M;* and a very small final residue. The saturation pressures of these fractions were compared by means of the differential manometer, *N*. During these measurements, the bulbs of the manometer which held the condensates were surrounded with a block of frozen mercury. After each comparative measurement, the positions of the condensates were interchanged to eliminate errors of capillarity.

The following observations were made:

1. No difference in pressure was observed when comparing the final residue with the middle fraction.
2. The saturation pressure of the initial distillate was 0.06 mm higher than that of the middle fraction.
3. The saturation pressure of the initial distillate was 0.06 mm higher than that of the final residue. Each of these observations represents the average of 10 determinations. These data indicate the absence of impurities of higher boiling points, and the presence of traces of impurities of lower boiling points.

[5] For complete details see, Martin Shepherd, BS J. Research **12**, 185 (1934) RP643.

The amount of any suspected impurity may be estimated from the equation [6]

$$X_B = \frac{\Delta_p}{p^\circ_B - p^\circ_A},$$

where

X_B = mole fraction of impurity present.
Δp = differential saturation pressure observed with the manometer.
p°_B and p°_A = the saturation pressure of the impurity and the oxygen, each in the pure state.

If the impurity had been nitrogen, the data would account for the presence of 0.00003 mole fraction. The amount of nitrogen actually present would be slightly higher than indicated by this computed value. There is no reported temperature-composition diagram of the system nitrogen-oxygen under the conditions existing during the isothermal distillation employed in this test of purity; therefore, an exact calculation of the amount of nitrogen cannot be made. However, the isothermal distillation may be expected to isolate more of the nitrogen in the initial distillate than is possible by means of an isobaric distillation at 760 mm. Furthermore, the data of Baly show only 2.2 mole percent of oxygen in the vapor phase at 78.0° K and 760 mm. This at once indicates the high concentration of nitrogen which may be expected in the initial distillate, and it can be expected that the comparison of the saturation pressure of this distillate with that of the middle cut or final residue will produce almost the full effect which a nitrogen impurity would cause. This may also argue the efficacy of distillation as a means of final purification; but unfortunately such is not the usual case, for the elimination of the last traces of nitrogen by this means requires repeated fractionation and the wasting of large amounts of oxygen. Those who have previously employed this means of purification have reported no data which would definitely establish, or even give comforting assurance of, the purity of the product obtained.

If the impurity had been hydrogen, the amount detectable would be very much less than the estimated amount of nitrogen.

V. SIGNIFICANCE OF THE IMPURITIES

This oxygen was prepared for a reference sample in connection with the maintenance of the International Temperature Scale at the National Bureau of Standards. The significance of the impurities detected, with particular respect to the measurement of saturation pressures, is accordingly important.

Since nitrogen and hydrogen are the only lower-boiling impurities to be expected, the effect of each should be calculated. The most unfavorable case to assume is that the impurities occuring in the initial distillate would also be present in the oxygen used to fill the saturation pressure thermometers. Actually, this was not the case, since the initial and final fractions were discarded; but if this assumption is made, the maximum possible error in the saturation pressures of oxygen would be 0.06 mm Hg, the Δ_p observed with the differential

[6] See eq 6 on page 191 of BS J. Research **12**, (1934) RP643.

manometer. Such an error would actually never occur, since the measurements of saturation pressure in the thermometer do not magnify the effect of the impurity in the same manner as in the test for purity. Furthermore, had the impurity been hydrogen, almost all of it would have been discarded with the initial distillate and through the pump just prior to filling the saturation pressure thermometers (see following section of this paper). On the other hand, if the impurity had been nitrogen, it would not have been entirely discarded with the isolation of the initial distillate and a subsequent distillation of the condensate from the tube, *M*. The effect of the nitrogen should therefore be estimated. This may be done by assuming 0.00003 mole fraction of nitrogen in oxygen, and computing the saturation pressure of the mixture by means of Raoult's law. When this is done, it will be seen that this small amount of nitrogen will alter the saturation pressure of pure oxygen by 0.01 mm. Since this represents a reproducibility not ordinarily attained in the measurement of the saturation pressures of oxygen in the region of its normal boiling point, the oxygen prepared may be considered satisfactory for the purpose intended.

VI. FINAL TREATMENT AND TRANSFER OF OXYGEN TO THE SATURATION PRESSURE THERMOMETER

The initial distillate and the final residue obtained during the test for purity were discarded through the pump. The oxygen contained in the tube, *M*, was then distilled, a few milliliters being discarded through the pump. This distillation would effectively remove traces of hydrogen and some nitrogen. The test for purity did not indicate the necessity of this additional procedure, but it was performed as an additional precaution. Approximately 18 ml of liquid oxygen then remained, and was isolated in the tube, *M*.

The graduated tube, *K*, and the saturation pressure manometer, *L*, were evacuated with the same care used in outgassing the apparatus prior to the preparation of the oxygen. The connections to *L* were heated during this evacuation, and drastically flamed at the constriction where the thermometer was to be sealed off.

The technique used in filling the thermometer was designed to eliminate gases driven from the glass at the time the thermometer was sealed off. Oxygen was transferred from *M* to *K* by immersing the former in a bath of liquid oxygen and the latter in a bath of liquid air.

The amount collected in *K* was 0.2 ml (of liquid) in excess of the amount necessary to fill the thermometer to a pressure of 5 atmospheres (of gas) at room temperature. This oxygen was then condensed in the thermometer. The condensing bulb of the thermometer was now immersed in liquid oxygen, and the tube *K*, in liquid air. The flow of oxygen was consequently *from* the thermometer *to* the tube, *K*. While the excess of 0.2 ml of liquid oxygen was being condensed back into *K*, with vapor flowing from the thermometer, the constriction joining the two was fused shut. Thus, gases driven from the fused glass were carried away from the thermometer.

WASHINGTON, August 25, 1938.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1183

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REPRODUCIBILITY OF SILVER-SILVER HALIDE ELECTRODES[1]

By John Keenan Taylor and Edgar Reynolds Smith

ABSTRACT

Tests of the reproducibility in potential of the electrolytic, thermal-electrolytic, and thermal types of silver-silver chloride, silver-silver bromide, and silver-silver iodide electrodes, in both acid and neutral solutions, are reported. All of these silver-silver halide electrodes show an aging effect, such that freshly prepared electrodes behave as cathodes towards electrodes previously aged in the solution. They are not affected in potential by exposure to light, but the presence of oxygen disturbs the potentials of the silver-silver chloride and silver-silver bromide electrodes in acid solutions, and of the silver-silver iodide electrodes in both acid and neutral solutions. Except in the case of the silver-silver iodide electrodes, of which the thermal-electrolytic type seems more reliable than the electrolytic or the thermal type, the equilibrium potential is independent of the type, within about 0.02 mv.

CONTENTS

	Page
I. Introduction	307
II. Apparatus and materials	308
III. Silver-silver chloride electrodes	308
IV. Silver-silver bromide electrodes	310
V. Silver-silver iodide electrodes	313

I. INTRODUCTION

In a previous investigation on the reproducibility of the silver-silver chloride electrode in neutral solution of potassium chloride,[2] a significant aging effect, first noted by MacInnes and Parker,[3] was measured and discussed. The origin of this aging effect was traced to concentration-polarization. It was found that freshly prepared electrodes always behave as cathodes towards aged electrodes. The initial difference in potential sometimes exceeds a millivolt, but when sufficient time is allowed, the electrolytic, thermal-electrolytic, and thermal types of the silver-silver chloride electrode finally attain the same potential, within about 0.02 mv, irrespective of the presence or absence of light and of air dissolved in the solution.

In this investigation the work on the reproducibility of silver-silver chloride electrodes was extended to include measurements of the effect of aging and of the effect of oxygen, in acid solutions. In addi-

[1] A part of the material included in this paper was submitted as a thesis by J. K. Taylor in partial fulfillment of the requirements for the degree of Master of Science at the University of Maryland. The interest and advice of Prof. M. M. Haring are gratefully acknowledged.

[2] E. R. Smith and J. K. Taylor, J. Research NBS **20**, 837 (1938) RP1108.

[3] D. A. MacInnes and K. Parker, J. Am. Chem. Soc. **37**, 1445 (1915).

tion, silver-silver bromide and silver-silver iodide electrodes were studied with respect to aging, the effect of oxygen, and the influence of light, in both neutral and acid solutions.

II. APPARATUS AND MATERIALS

The measurements were made with the same apparatus, including the potentiometer, standard cell, galvanometer, thermostat, and vessels for the electrodes used in the previous work with silver-silver chloride electrodes.[4]

Potassium bromide and potassium iodide of reagent grade were recrystallized before use. Silver bromate was prepared by mixing solutions of silver nitrate and potassium bromate. The precipitated silver bromate was washed repeatedly and finally recrystallized from water. Silver iodate was prepared similarly from silver nitrate and potassium iodate, and was washed repeatedly before use. Hydrochloric and hydrobromic acids were prepared by diluting acids of reagent quality and adjusting the concentration to 0.05 *N*.

Nitrogen, for the removal of oxygen from the solutions, was freed from oxygen by passage through hot copper in a tubular electric furnace. It was then passed through solutions of sodium hydroxide, dilute sulfuric acid, and finally through a solution of the same composition as that in the cell.

III. SILVER-SILVER CHLORIDE ELECTRODES

It has been demonstrated previously [5] that the aging effect results from concentration-polarization. This effect should, therefore, occur in acid solutions as well as in neutral solutions, and it is important to know how much time should be allowed after the preparation of silver-silver chloride electrodes to insure the attainment of their equilibrium potential.

The aging effect was found to occur in oxygen-free acid solutions and was measured by the following procedure. Eight silver electrodes of the thermal type and a large silver-silver chloride electrode were placed in a cell of the design shown in figure 1, containing 0.05 *N* hydrochloric acid solution. Nitrogen was bubbled continuously through the cell (except during the measurements) to remove oxygen, and two of the silver electrodes were chloridized, using the large silver-silver chloride electrode as a cathode. In this way, the silver-silver chloride electrodes were formed without contact with oxygen and without change in the composition of the solution. After waiting several days to allow the freshly formed electrodes to age, a second pair of the silver electrodes was chloridized and then compared in potential with the first two. On succeeding days the remaining two pairs of electrodes were chloridized and compared with the two aged electrodes. In figure 2 the points on the curve represent the average values of potential difference for each pair, with reference to the aged pair at the given time. The new electrodes were initially positive to aged electrodes, rapidly approached the latter in potential during the first several hours, and finally, after a period of from 1 to 2 days, attained an equilibrium potential in agreement with that of the older electrodes.

[4] E. R. Smith and J. K. Taylor, J. Research NBS **20**, 837 (1938) RP1108.
[5] See footnote 4.

This behavior is practically identical with that found for these electrodes in neutral solution.

In the previous paper, oxygen was shown to have no significant effect on the potential of the silver-silver chloride electrode in neutral solutions, but it has long been known that in acid solutions the potential is disturbed by the presence of oxygen. Güntelberg [6] attributed this disturbance to the reaction

$$2Ag + 2HCl + \tfrac{1}{2} O_2 = 2AgCl + H_2O. \qquad (1)$$

If this reaction causes the disturbance, then in the presence of oxygen there should be a slight decrease in the concentration of hydrochloric acid within the interstices of the coating of silver chloride which envelops the silver, and such a decrease should cause an oxygen-saturated electrode to act as a cathode towards an oxygen-free electrode. The disturbing effect of oxygen in acid solution was confirmed, and a direct measurement of its sign and magnitude was accomplished in the following way:

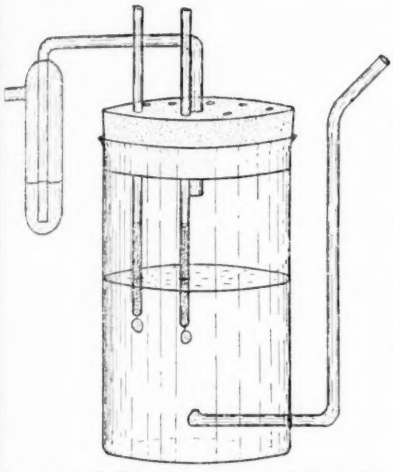

FIGURE 1.—*Cell for comparison of electrodes.*

Two cells, of the type shown in figure 1, each containing seven thermal silver-silver chloride electrodes immersed in 0.05 *N* hydrochloric acid solution, were connected by an inverted Y-tube of 5-mm bore, through which the cells could be connected at will by drawing up solution from them to form a liquid junction. After passing nitrogen through each cell to remove oxygen, the largest difference in potential between any two electrodes in each set was 0.02 mv and, on making the junction between the cells, the average potential difference between the electrodes in cell 1 and those in cell 2 was 0.05 mv. Those in cell 1 were cathodic by this amount with respect to those in cell 2. The junction between the cells was then disconnected and oxygen was bubbled through cell 1 while nitrogen was again passed through cell 2. After saturation with oxygen, the electrodes in cell 1 varied erratically in potential with respect to each other by as much as 0.19 mv, and on reforming the junction the average difference in potential between cell 1 and cell 2 increased to 0.21 mv. Cell 1, saturated with oxygen, acted as a cathode toward cell 2. The oxygen was then swept out of cell 1, and its electrodes returned to their original agreement among themselves and with those of cell 2.

The magnitude of the effective change in concentration resulting from the reaction given by eq 1 can be estimated from a consideration of the cell

$$Ag|AgCl,\ HCl(C)|HCl(C-\delta),\ AgCl|Ag,$$

[6] E. Güntelberg, Z. physik. Chem. **123**, 199 (1926).

in which δ is the effective decrease in concentration of hydrochloric acid within the porous electrode in the oxygen-saturated solution. Since δ is small, the concentrations C and $C-\delta$ are nearly the same. Consequently, the variations in ionic mobilities between these concentrations may be assumed to be negligible, and the activity ratio may be taken as equal to the concentration ratio. The expression for the emf of the cell then becomes

$$E=2N_{\mathrm{H}}\left(\frac{RT}{F}\right)ln\frac{C}{C-\delta}, \tag{2}$$

in which N_{H} is the cation transference number, and the other symbols have their usual meanings. Since ln $C/C-\delta)>0$, $E>0$, and the oxygen-saturated electrode is the cathode. Substituting the measured value of E (0.00021 v) and the appropriate values of the other quantities [7] in eq 2, it is found that $\delta\simeq C/200$. This means that the reaction with oxygen caused a change in the effective concentration of acid

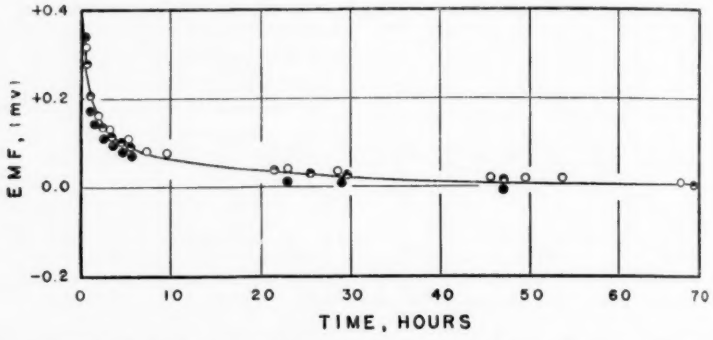

FIGURE 2.—*Aging effect with the thermal-electrolytic type of silver-silver chloride electrodes in 0.05 N air-free solution of hydrochloric acid.*

within the pores of the electrode of about 0.5 percent. The total amount of solution within the pores is, however, relatively so small that, after removal of the oxygen and reattainment of equilibrium with the bulk of the solution, the net change in concentration is insignificant, and the electrodes readily return to their initial potential. The figure of 0.5 percent is, of course, only an order of magnitude, since in any given case the value will depend on the time of contact, concentration of oxygen, and the porosity of the electrodes.

IV. SILVER-SILVER BROMIDE ELECTRODES

Silver-silver bromide electrodes of the electrolytic type were prepared by electroplating silver on rectangular pieces of platinum gauze, 0.5 by 1 cm, washing them for 10 days in frequently changed distilled water, to eliminate contamination by the plating solution,[8] and bromidizing them electrolytically in 1 N hydrobromic acid solution with a current of 4 ma per electrode for 1 hour. These electrodes were first soaked for 1 hour in 0.05 N potassium bromide solution and

[7] The cation transference number in 0.05 N HCl at 25° C is 0.829, according to L. G. Longsworth, J. Am. Chem. Soc. **54**, 2741 (1932).
[8] W. R. Carmody, J. Am. Chem. Soc. **51**, 2901 (1929).

then placed in a cell containing 0.05 *N* potassium bromide solution. After 1 week, to allow for aging, during which time nitrogen was passed through the cell, their differences in potential were recorded.

Thermal-electrolytic electrodes were made by heating a paste of silver oxide and water, supported on spirals of platinum wire, and electrolytically coating the resulting porous beads of silver with bromide from a large silver-silver bromide electrode. The latter operation was performed after placing the electrodes in a second cell containing 0.05 *N* potassium bromide, through which nitrogen was passed. After allowing 1 week for aging, their differences in potential were measured.

Thermal electrodes were prepared by heating to decomposition in an electric furnace a paste of silver oxide and silver bromate in water, supported on spirals of platinum wire.[9] These were placed together in a third cell containing 0.05 *N* potassium bromide solution, from which oxygen was excluded by nitrogen, and after 1 week their differences in potential were recorded.

The results of the reproducibility tests on these three types of silver-silver bromide electrodes, exposed to light in neutral (0.05 *N*) air-free potassium bromide solution, are shown in table 1. From this table it is seen that under these conditions the individual electrodes of any one type agree among themselves within a few hundredths of a millivolt.

TABLE 1.—*Reproducibility of different types of silver-silver bromide electrodes exposed to light in neutral air-free 0.05 N potassium bromide solution*

Electrode number	Electrolytic type	Thermal-electrolytic type	Thermal type
	mv	*mv*	*mv*
1–2	0.00	−0.03	+0.01
1–3	+.04	+.02	.00
1–4	+.05	.00	.00
1–5	−.01	+.01	−.04
1–6	−.02	.00	−.04
1–7	−.02	+.02	.00
Average deviation	0.02	0.01	0.02

To determine the agreement of the different types, six electrolytic and six thermal silver-silver bromide electrodes were compared with a group of five thermal-electrolytic electrodes. The results are given in table 2 and show that the different types attain the same final value of potential within a few hundredths of a millivolt.

[9] A. S. Keston, J. Am. Chem. Soc. **57**, 1671 (1935).

TABLE 2.—*Comparison of different types of silver-silver bromide electrodes in neutral, air-free 0.05 N potassium bromide solution*

Electrode number	Description [1]	Potential difference
		mv
1-2	*TE-TE*	0.00
1-3	*TE-TE*	−.01
1-4	*TE-TE*	−.01
1-5	*TE-TE*	−.01
1-6	*TE-E*	.00
1-7	*TE-E*	+.04
1-8	*TE-E*	+.05
1-9	*TE-E*	−.01
1-10	*TE-E*	−.02
1-11	*TE-E*	−.02
1-12	*TE-T*	+.01
1-13	*TE-T*	.00
1-14	*TE-T*	.00
1-15	*TE-T*	−.04
1-16	*TE-T*	−.04
1-17	*TE-T*	.00

[1] *E*, *TE*, and *T* symbolize electrolytic, thermal-electrolytic, and thermal types, respectively.

The time required for silver-silver bromide electrodes to come to equilibrium was determined by measuring the aging effect according

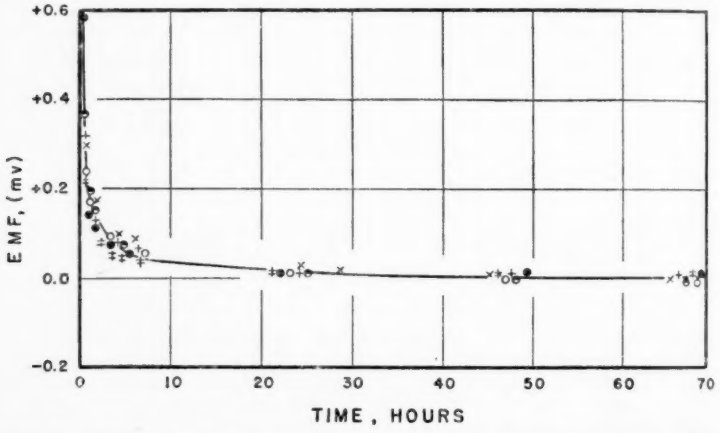

FIGURE. 3.—*Aging effect with the thermal-electrolytic type of silver-silver bromide electrodes in 0.05 N air-free solution of potassium bromide.*

to the procedure used with the silver-silver chloride electrodes. The results obtained with the thermal-electrolytic type, in air-free 0.05 *N* potassium bromide solution, are shown in figure 3. The several kinds of crosses represent the measurements with electrodes prepared and measured with light excluded. The several kinds of circles represent the results with electrodes exposed to light. It is apparent that light has no effect on the aging of these electrodes. Also, that light has no effect on their equilibrium potential was shown by interchanging some of the electrodes between the blackened and the transparent cell. This interchange was made in a dark room and, on comparing the potentials of the light-protected and light-exposed electrodes, no significant differences were found.

The aging of the thermal type of silver-silver bromide electrodes in neutral air-free solution of potassium bromide is shown in figure 4. These data were obtained by placing electrodes, freshly prepared on succeeding days, in a cell containing aged electrodes, and, at definite intervals of time, comparing the potentials of the newer electrodes with those of the aged ones.

The effect of oxygen on the potential of silver-silver bromide electrodes was measured by the procedure used for the silver-silver chloride electrodes. In neutral solution (0.05 *N* KBr) no effect was observed, but in acid solution (0.05 *N* HBr) a marked effect was found. In the latter case, with seven thermal-electrolytic electrodes in each of the two cells connected by the inverted Y-tube, an average difference of 0.01 mv was obtained between the electrodes in cell 1 and those in cell 2, when oxygen was excluded from both. When oxygen was passed into cell 1, the individual electrodes varied errati-

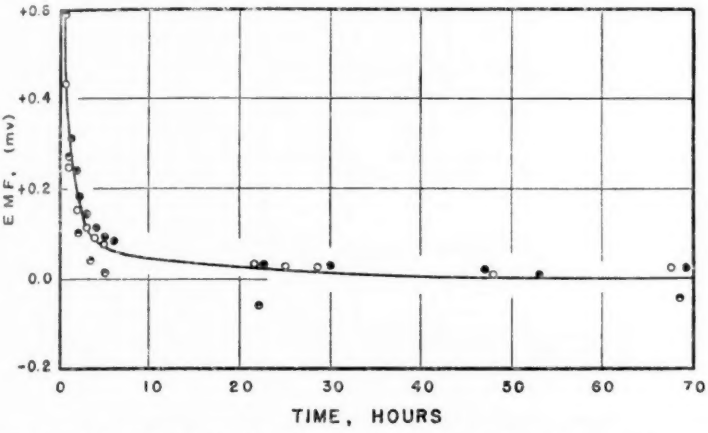

FIGURE 4.—*Aging effect with the thermal type of silver-silver bromide electrodes in 0.05 N air-free solution of potassium bromide.*

cally in potential with respect to each other by as much as 0.23 mv and the average difference in potential between electrodes in cell 1 and cell 2 became 0.30 mv. The oxygen-saturated set acted as a cathode toward the oxygen-free set of electrodes. After removal of the oxygen, the electrodes returned to their initial agreement. The influence of oxygen is thus in the direction to be expected from the reaction.

$$2Ag+2HBr+1/2\ O_2=2AgBr+H_2O, \qquad (3)$$

which causes an effective decrease in the concentration of the acid within the pores of the electrode.

V. SILVER-SILVER IODIDE ELECTRODES

A number of sets of the electrolytic, thermal-electrolytic [10] and thermal [11] types of silver-silver iodide electrode were prepared by methods analogous to those used for the chloride and bromide electrodes. They were tested for reproducibility and agreement of the different types. The thermal-electrolytic type showed a reproduci-

[10] G. Jones and M. L. Hartman, J. Am. Chem. Soc. **37**, 756 (1915).
[11] B. B. Owen, J. Am. Chem. Soc. **57**, 1526 (1935).

bility of about 0.02 mv, comparable to that of the other halide electrodes, but the thermal and the electrolytic types were not as satisfactory. Occasionally, self-consistent groups of the latter two types were obtained, but more often the reproducibility was no better than 0.1 to 0.2 mv, particularly between electrodes prepared at different times. When the three types were intercompared, the thermal and the electrolytic type were always positive (i. e., cathodic) toward the thermal-electrolytic type by 0.1 to 0.2 mv. Since the cause of this behavior was not discovered, the experiments on the effects of light, oxygen, and aging on the potential of the silver-silver iodide electrode were confined to the thermal-electrolytic type.

The aging effect of the silver-silver iodide electrodes in neutral solution of 0.05 *N* potassium iodide in the presence and absence of light was measured according to the procedure used for the thermal-

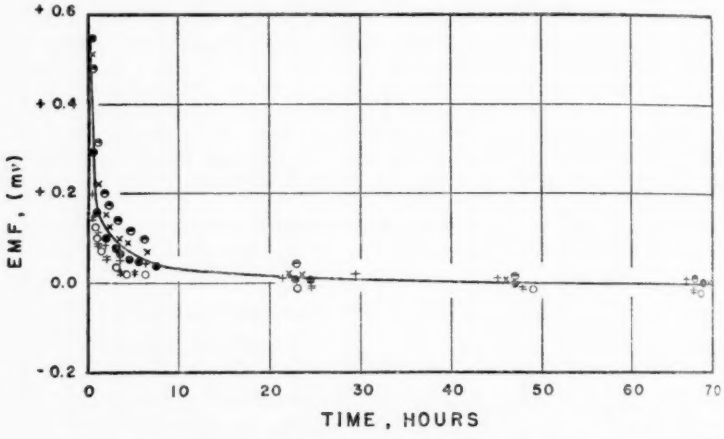

FIGURE 5.—*Aging effect with the thermal-electrolytic type of silv r-silver iodide electrodes in 0.05 N air-free solution of potassium iodide.*

electrolytic type of silver-silver chloride and silver-silver bromide electrodes. The results are shown in figure 5, in which the circles and crosses of various types represent, respectively, electrodes protected from and exposed to light. By interchanging electrodes between the blackened and the transparent cell, the interchange being made in a dark room, it was found that all the electrodes had the same potential within about 0.02 mv.

The effect of oxygen on the potentials of the silver-silver iodide electrodes was tested in neutral solution of 0.05 *N* potassium iodide, using two cells connected by an inverted Y-tube, as in the tests with the other electrodes. With oxygen excluded from both cells, the average difference in potential between the electrodes in cell 1 and in cell 2 was 0.02 mv. As soon as oxygen was admitted to cell 2, its electrodes behaved erratically and became, on the average, 1.5 mv positive with respect to the electrodes in the oxygen-free cell. This effect is so marked in neutral solutions that it was considered unnecessary to make the same test in solutions of hydriodic acid, since the instability of the latter substance in the presence of oxygen is well known.

WASHINGTON, December 20, 1938.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1184

Part of Journal of Research of the National Bureau of Standards, Volume 22, March 1939

2,6-DIMETHYLHEPTANE: ITS SYNTHESIS, PROPERTIES, AND COMPARISON WITH AN ISONONANE FROM PETROLEUM [1]

By Joseph D. White,[2] Frank W. Rose, Jr.,[3] George Calingaert,[4] and Harold Soroos [4]

ABSTRACT

An isononane boiling at 135.2° C was tentatively identified as 2,6-dimethylheptane at the time of its isolation from a midcontinent petroleum. 2,6-Dimethylheptane has been synthesized by means of the Grignard reaction and the properties of a purified fraction compared with those of the isononane from petroleum. The properties of the isononane from petroleum are in good accord with those of 2,6-dimethylheptane. The properties of 2,6-dimethylheptane (extrapolated to a purity of 100.0 mole percent from measurements actually made on material of purity 99.6 mole percent) are as follows: Boiling point at 760 mm Hg, 135.21° ±0.02° C; freezing point in air, −102.95 ±0.10° C; density at 20° C, 0.70891 ±0.00003 g/ml; refractive index, n_D^{20} 1.40073±0.00005; critical solution temperature in aniline, 80.0° ±0.3° C.

CONTENTS

	Page
I. Introduction	315
II. Synthesis of 2,6-dimethylheptane	316
III. Physical properties of synthetic 2,6-dimethylheptane and its comparison with an isononane obtained from petroleum	316
IV. References	319

I. INTRODUCTION

The isolation from a midcontinent petroleum of an isomeric nonane boiling at 135.2° C has been described in an earlier paper by White and Rose [1].[5] The identification of the compound was attempted at the time, by comparing the physical constants of the hydrocarbon from petroleum with those reported for the few nonanes known to boil near 135° C. The compound had properties most nearly like those reported for 2,6-dimethylheptane [2, 3], but the agreement was not sufficient, in the absence of knowledge concerning 19 of the 35 structurally possible isomers of C_9H_{20}, to make the identification complete.

The indication from the correlation of physical properties that the compound might be 2,6-dimethylheptane was in keeping with a suspected dimethylheptane structure, a supposition based on the fact that all of the isoparaffinic hydrocarbons previously isolated from the

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Formerly Research Associate at the National Bureau of Standards, representing the American Petroleum Institute; now with the W. C. Hardesty Co., Dover, Ohio.

[3] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

[4] Research Laboratory, Ethyl Gasoline Corporation, Detroit, Mich.

[5] Figures in brackets indicate the literature references at the end of this paper.

petroleum have been mono- or dimethyl derivatives and on the further fact that the isomeric nonane in question boiled at a much lower temperature than any of the monomethyloctanes. This view was supported by a study of the diagrams, prepared by Calingaert and Hladky, correlating the physical properties of the alkanes with their molecular structure [4].[6]

Moreover, a study of the near infrared absorption spectra in the region 5,400 to 8,900 cm^{-1} (1.82 to 1.12 μ) showed the absorption characteristic of isoparaffins. For this region, the salient features of the absorption of branched or methylated paraffins have been discussed by Liddel and Kasper [5] and later by Rose [6]. A mathematical analysis of the molal absorption index, according to the method recently described by one of the authors [7], yielded the following values for the number of component structural groups in the molecule: $-CH_3$, 4 ± 0.4; $-CH_2$, 3 ± 0.4; $-CH$, 2 ± 0.6. This indicated that the isononane was a dimethylheptane or a methylethylhexane in which the branches are not attached to the same carbon atom.[7]

II. SYNTHESIS OF 2,6-DIMETHYLHEPTANE

Synthetic 2,6-dimethylheptane was prepared and purified by the general method described earlier by Calingaert and Soroos [8]. In this case, isobutyl magnesium bromide was coupled with ethyl formate, producing 2,6-dimethylheptanol-4 (bp/18 mm, 80.0 to 81.50° C; d_4^{20}, 0.810; n_D^{20}, 1.4232) in a 74-percent yield. This carbinol was hydrogenated in three steps, giving a 90-percent yield of crude alkane, which was then treated with 98-percent sulfuric acid, washed, dried, refluxed over sodium-potassium alloy, and finally fractionated carefully in a column packed with crushed carborundum.

III. PHYSICAL PROPERTIES OF SYNTHETIC 2,6-DIMETHYLHEPTANE AND ITS COMPARISON WITH AN ISONONANE OBTAINED FROM PETROLEUM

The physical properties of the synthetic material purified by distillation were determined. The values obtained are listed in table 1 under the designation "best by distillation."

[6] These diagrams indicate the boiling points and molecular volumes (densities) of not only the known members of groups of isomeric paraffins but also of several of the unknown members by interpolation and extrapolation of curves for homologous series.

[7] The details and experimental data for this analysis are given in the paper cited [7].

TABLE 1.—*Physical properties of two preparations of synthetic 2,6-dimethylheptane and of the isononane from petroleum*

Physical property	Isononane from petroleum	Synthetic 2,6-dimethylheptane	
		"Best by distillation"	"Best by distillation and crystallization"
Normal boiling point, °C	[a] 135.208 ±0.003	[a] 135.210 ±0.003	[b]
Pressure coefficient, dt/dp °C/mm Hg		0.0490	
Initial freezing point in air, °C	[c] −103.24 ±0.02	−104.1 ±0.03	[c] −103.04 ±0.02
Density at 20° C, g/ml	[d] 0.70963 ±0.00002	[d] 0.70949 ±0.00002	[d] 0.70894 ±0.00002
Temperature coefficient, dD/dt, per degree			[e] −0.00079
Refractive index, n_D^{20}	[f] 1.40115 ±0.00005	[f] 1.40095 ±0.00005	[f] 1.40075 ±0.00005
Temperature coefficient, dn/dt, per degree			[e] −0.00049
Critical solution temperature in aniline, °C	[g] [h] 79.9 ±0.2	[g] 80.3 ±0.2	[g] 80.0 ±0.2
Purity, mole percent	[i] 98.8	[i] 95	[i] 99.6

[a] Determined by E. R. Smith of the Physical Chemistry Section of this Bureau in a standard Swietoslawski ebulliometer [11].
Difference in boiling and condensation points: Petroleum sample, 0.033° C; synthetic ("best by distillation"), 0.008°C. It should be noted that these results are misleading if used as a criterion of purity, because the synthetic preparation before crystallization contained four times the amount of the impurity in the isononane from petroleum.
[b] Not measured, assumed to be the same as for the preparation before crystallization.
[c] Initial freezing point. Data obtained with a platinum resistance thermometer of 25 ohms.
[d] Determined by the Division of Weights and Measures of this Bureau.
[e] From measurements at 20° and 25° C.
[f] Determined on a calibrated Abbe refractometer (Valentine design).
[g] Comparative values. At this temperature the mixture contained 37 mole percent of the hydrocarbon.
[h] The previously reported [1] value, 81.2 ±0.5°C, is considered to be in error because of lack of stirring during the observation.
[i] Calculated from the slope of the freezing curve (see text).

In figure 1, curve *III* (broken) is the time-temperature freezing curve for the synthetic 2,6-dimethylheptane, "best by distillation."

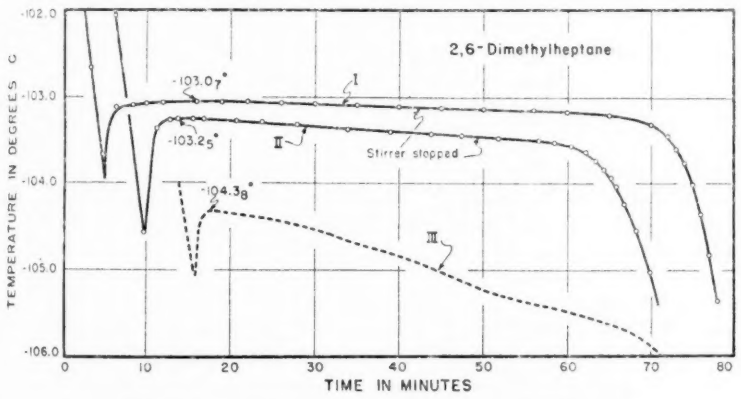

FIGURE 1.—*Cooling curves of 2,6-dimethylheptane.*

Curve *I*, synthetic, purified by distillation and crystallization; curve *II*, from petroleum; curve *III*, synthetic, purified by distillation alone. Curves *II* and *III* are the same, respectively, as curves *I* and *II* in figure 2. The time scale for curves *II* and *III* is twice the actual scale.

The slope of the curve during the freezing interval indicated that the material was not of the highest purity, and consequently the distilled synthetic material was further purified by crystallization. A 200-ml portion was twice crystallized from its solution in dichlorodifluoro-

methane, the crystals being separated from the liquid phase by centrifuging. There was obtained a 50-ml fraction which was degassed and filtered through silica gel to remove the last traces of solvent. The values of the properties of the highly purified synthetic 2,6-dimethylheptane are listed in table 1 under the heading, "best by distillation and crystallization." Hereafter, this preparation is referred to as the "best" synthetic material.

The behavior during freezing of the "best" synthetic material is shown in curve *I* of figure 1. The highest observed point on curve *I* is $-103.0_7°$ C, and the initial freezing point is $-103.0_5°$ C. From the initial freezing point and the slope of the curve, the freezing point of the substance 100.0 percent pure is estimated [8] to be $-102.95°$ C.

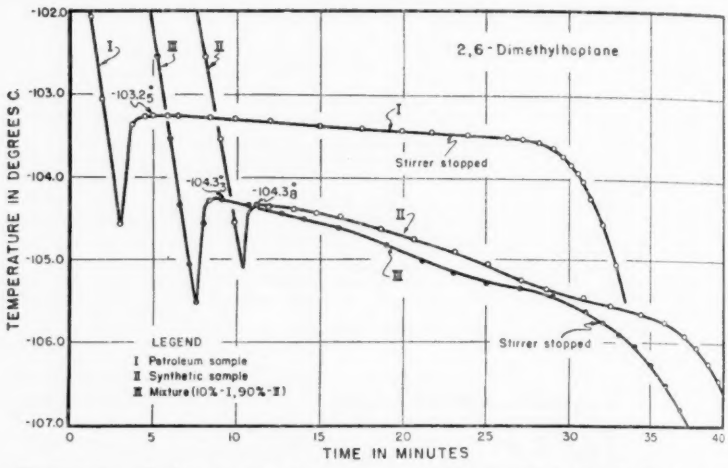

FIGURE 2.—*Cooling curves of various preparations of 2,6-dimethylheptane.*

Using a value of 2.5 ±0.2 kcal/mole for its heat of fusion,[9] the purity of the "best synthetic" material was calculated to be 99.6 ±0.1 mole percent.

The properties previously reported for the isononane from petroleum [1] are listed in table 1. A calculation of the purity, made in a manner similar to that for the synthetic 2,6-dimethylheptane, yielded a value of 98.8 ±0.2 mole percent.

The cooling behavior of a mixture containing 10 parts of the petroleum hydrocarbon and 90 parts of synthetic 2,6-dimethylheptane ("best by distillation") was studied. Time-temperature freezing curves of the mixture and of the two component materials are shown in figure 2. The freezing point of the mixture, as indicated in curve *III*, lay between that of the hydrocarbon from petroleum and that of the synthetic preparation (curves *I* and *II*, respectively), and was proportionately nearer to the freezing point of the latter.

[8] The computations are based on the assumptions that the midpoint of the freezing interval indicates the point at which the material is half frozen [9], that at the midpoint where the mixture is half frozen the concentration of impurity in the liquid has doubled, and that the impurity is soluble in the liquid phase but not in the solid phase.

[9] From data on the heats of fusion of other paraffin hydrocarbons, the heat of fusion of 2,6-dimethylheptane was estimated to be 2.7±0.4 kcal/mole. In connection with another investigation [12], the heat of fusion of the isononane from petroleum was calculated to be 2.5 ±0.2 kcal/mole, from values of the molecular depression of the freezing point produced by the addition, to the isononane, of known quantities of ethylcyclohexane.

TABLE 2.—*Values of the properties* [a] *of the hydrocarbon, 100.0 mole percent pure, obtained by extrapolation of measurements actually made on synthetic 2,6-dimethylheptane, 99.6 mole percent pure, and on the isononane from petroleum, 98.8 mole percent pure*

Physical property	Synthetic	Petroleum
Normal boiling point, °C	135.21 ±0.02	135.21 ±0.02
Freezing point in air, °C	[b] −102.95 ±0.03	[b] −103.04 ±0.06
Density at 20° C, g/ml	0.70891 ±0.00003	0.70876 ±0.00010
Refractive index, n_D^{20}	1.40073 ±0.00005	1.40079 ±0.00010

[a] For values of the coefficients of these properties with temperature or pressure see table 1.
[b] These uncertainties are relative. It is estimated that the values are good to ±0.10° C (including uncertainties in the method and in thermometry).

Table 2 gives values of the properties of the hydrocarbon, 100.0 mole percent pure, obtained by extrapolation of measurements actually made on synthetic 2,6-dimethylheptane, 99.6 mole percent pure, and on the isononane from petroleum, 98.8 mole percent pure. The extrapolations were made on the assumptions that the impurity in the synthetic material was normal nonane and that in the isononane from petroleum was a nonanaphthene [1, 10, 12], and that, within the small range involved, the values of density and refractive index are linear functions of the mole fractions of the components. The freezing point was calculated according to the procedure previously mentioned. The nature of the impurities was deduced from the manner of preparation and purification of the respective materials. Conservative estimates of the uncertainties have been assigned to the values, there being included in the uncertainty one-third of the amount of extrapolation of the freezing point and one-tenth of the amount of the extrapolation of the density and refractive index. The values from the two preparations are substantially in agreement within the assigned limits of uncertainty.

The authors express thanks to O. R. Wulf of the Fertilizer Investigations Laboratory of the Bureau of Chemistry and Soils, United States Department of Agriculture, through whose courtesy the infrared absorption spectra were measured, and to F. D. Rossini, director of this project, for his advice and encouragement.

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WASHINGTON, December 28, 1938.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1185

Part of Journal of Research of the National Bureau of Standards, Volume 22, March 1939

SEPARATION OF HYDROCARBONS OF HIGH MOLECULAR WEIGHT BY ADSORPTION ON SILICA GEL[1]

By Charles B. Willingham[2]

ABSTRACT

Data are presented on the separation of different types of hydrocarbons of high molecular weight by adsorption on silica gel. A sharp separation of 5-(7-tetrahydronaphthyl)-docosane from 5-(2-decahydronaphthyl)-docosane, and *n*-dotriacontane from 1-(*p*-diphenyl)-octadecane was obtained. Some separation of 1-(*p*-diphenyl)-octadecane from 5-(7-tetrahydronaphthyl)-docosane was found, but the separation was not as sharp as with the two preceding mixtures. No separation of a mixture of *n*-dotriacontane and 5-(2-decahydronaphthyl)-docosane was found.

The capacity of 20 g of silica gel to adsorb preferentially the more aromatic components of these mixtures was found to be 1.8, 3.3, and 0.8 g, respectively, for the first three mixtures listed above.

CONTENTS

	Page
I. Introduction	321
II. Apparatus and material	321
III. Procedure	322
IV. Experimental results	323
V. References	327

I. INTRODUCTION

Preferential adsorption by silica gel has been used for several years for separating mixtures of hydrocarbons of both the gasoline [1][3] and lubricating oil [2] fractions of petroleum. The study made by Mair and White [3] showed that, for hydrocarbons similar to those occurring in the gasoline fraction of petroleum (C_5 to C_{10}), adsorption with silica gel is effective in removing completely small amounts of aromatic hydrocarbons from their mixtures with paraffin and naphthene hydrocarbons, and further, gave information concerning the efficiency and capacity of the gel for such separation. However, as no data have heretofore been reported concerning the effectiveness of silica gel for separating hydrocarbons of high molecular weight, it is the purpose of the present note to report such information.

II. APPARATUS AND MATERIAL

The apparatus used was essentially the same as that described by Mair and White [3], except that both the tube containing the silica

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[2] Research Associate at the National Bureau of Standards, representing the American Petroleum Institute.

[3] Numbers in brackets indicate the literature references at the end of this paper.

gel and the receiver were equipped with a heating jacket, as shown in figure 1. Because of the high melting point of some of the hydrocarbons, several of the experiments were performed at about 100° C, and for the same reason, the refractive indices, used to mark the extent of the separation (as illustrated in fig. 2), were determined at 80° C.

The silica gel used was marked "150–F–850" (40 to 200 mesh).[4]

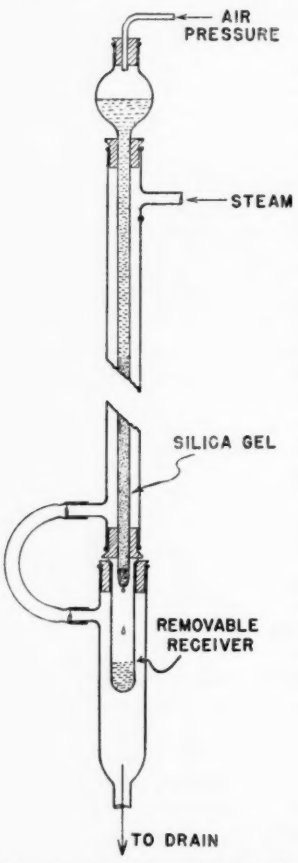


FIGURE 1.—*Apparatus for filtering hydrocarbons of high molecular weight through silica gel.*

Three of the synthetic hydrocarbons used in this work, 5-(7-tetrahydronaphthyl)-docosane, 5-(2-decahydronaphthyl)-docosane, and 1-(*p*-diphenyl)-octadecane, were kindly furnished by L. A. Mikeska [4] of the Standard Oil Development Co.; the other, *n*-dotriacontane, was prepared by Y. Delcourt [5], and further purified at this laboratory by distillation in high vacuum.

In order to ascertain whether these synthetic hydrocarbons were sufficiently pure for the present experiments, each of them was first filtered through silica gel in the same manner as in the experiments with the mixtures. The refractive indices of all the fractions for each compound, with the exception of those from 5-(2-decahydronaphthyl)-docosane, were substantially constant and the same as that for the compound before filtration. This indicated that no fractionation occurred during passage through the gel. The compound 5-(2-decahydronaphthyl)-docosane, however, showed some fractionation, and fractions with refractive indices, n_D^{25}, varying from 1.4926 to 1.4932, were obtained before a constant value (1.4932) was realized.

III. PROCEDURE

The procedure adopted for the present experiments was as follows: To a weighed amount (20 to 25 g) of one component in a small flask was added a weighed amount of the second component to produce a mixture of the desired concentration (10 to 20 percent by weight in the present experiments). The components were then melted by placing the flask on the steam bath, and thoroughly agitated to insure homogeneity. After the refractive index had been determined, the mixture was transferred to the filtering tube and allowed to filter, under an air pressure of about 4 lb./in.^{2} through 50 cm (approximately 20 g) of loosely packed gel.

In all of the experiments except No. 1, the filtering tube and receiver were kept at approximately 100° C by passing steam through

[4] This was purchased from the Davison Chemical Corporation, Silica Gel Division, Baltimore, Md.

the jacket. A small gas flame from a bunsen burner was used, as needed, to keep the material in the upper bulb liquid. The filtrate was collected in a number (7 to 9) of small fractions, and the refractive index of each was determined.

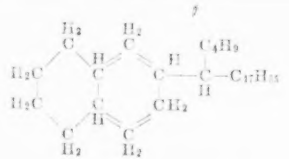
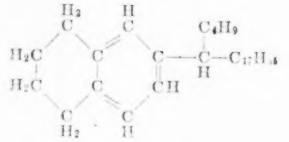
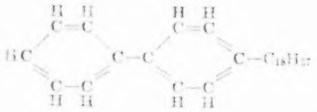
The previously used technique [3] of displacing the adsorbed material from the gel with water could not be used in the present experiments because of the higher temperature. Instead, toluene, which boils at 110° C and is highly adsorbed by silica gel, was passed through the column to displace the adsorbed hydrocarbons of high molecular weight, which were thus obtained in solution with the excess toluene. The bulk of the toluene was subsequently separated from the wanted hydrocarbons by simple distillation, with the last traces of toluene being removed at 120° to 130° C by sweeping with a small stream of carbon dioxide.

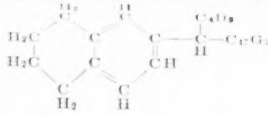
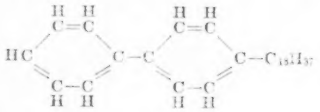
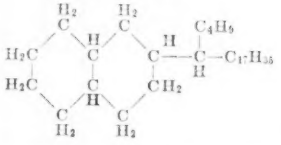
IV. EXPERIMENTAL RESULTS

Experiment 1 (see table 1), performed at about 25° C (room temperature), shows the recovery of substantially pure 5-(7-decahydronaphthyl)-docosane, a naphthene or cycloparaffin hydrocarbon, from its mixture with the corresponding aromatic hydrocarbon. The separation was sharp, and the capacity of the gel was found to be 1.8 g of aromatic hydrocarbon adsorbed by 20 g of gel.[5]

[5] This capacity does not differ greatly from that reported by Mair and White [3] for hydrocarbons of low molecular weight; namely, 5.6 g of o-xylene adsorbed by 50 g of gel from a 10-percent solution of it with n-nonane, and 5.2 g of toluene adsorbed by 50 g of gel from a 10-percent solution of it with n-heptane.

TABLE 1.—*Experimental results*

Experiment No.	Hydrocarbons: Name	Hydrocarbons: Formula	Weight	Refractive index $n_D^{80(s)}$: Hydrocarbons	Refractive index $n_D^{80(s)}$: Mixture	Weight of silica gel	Temperature of separation	Fractions: Number	Fractions: Weight	Fractions: Refractive index n_D^{80}
			g			g	°C		g	
1	5-(2-decahydronaphthyl)-docosane.		20.87	b1.4750	b1.4761	20.0	(25)	1-7	15.21	b1.4750
								8	2.04	b1.4755
								"Hold-up"	.....	Not recovered.
1	5-(7-tetrahydronaphthyl)-docosane.		2.60	b1.4932						
2	*n*-Dotriacontane	$CH_3(CH_2)_{30}CH_3$	23.85	1.4329	1.4430	18.0	100	1-5	14.50	1.4329
								6	3.90	1.4350
								7	3.53	1.4425
								8	2.15	1.4490
2	1-(*p*-Diphenyl)-octadecane		4.72	1.5031				"Hold-up"	3.60	1.4760

3	5-(7-tetrahydronaphthyl)-docosane.		27.68	1.4723					
					1.4777	21.0	100	1	0.62	1.4608
								2	2.21	1.4723
								3	2.82	1.4749
								4	3.56	1.4767
								5	4.42	1.4781
								6	4.51	1.4779
								7	5.59	1.4782
								8	2.06	1.4780
3	1-(*p*-Diphenyl)-octadecane		5.54	1.5031				9	----	1.4793
								"Hold-up"	3.20	1.4823
4	*n*-Dotriacontane	$CH_3(CH_2)_{30}CH_3$	22.53	1.4329						
					1.4340	20.0	100	1–7	21.7	[a]1.4340
								"Hold-up"	----	1.4340
4	5-(2-decahydronaphthyl)-docosane.		2.50	1.4550						

[a] Because of the difficulty experienced in maintaining this high temperature, the refractive indices reported here are considered accurate only to ±0.0002.
[b] These refractive indices were determined at 25° C.
[c] This value is the average for the first 7 fractions, the greatest deviation being ±0.0002.

A sharp separation was obtained also in experiment 2, where substantially pure *n*-dotriacontane, a paraffin hydrocarbon, was recovered from its mixture with the aromatic hydrocarbon 1-(*p*-diphenyl)-octadecane. A graphical representation of this separation is shown in figure 2. In this experiment, the capacity of the gel was much greater than in experiment 1, being 3.3 g of aromatic hydrocarbon adsorbed by 20 g of gel from a solution containing 16.5 percent of the aromatic hydrocarbon.

Experiment 3 was performed with a mixture of 5-(7-tetrahydronaphthyl)-docosane which contains 1 aromatic ring, and 1-(*p*-di-

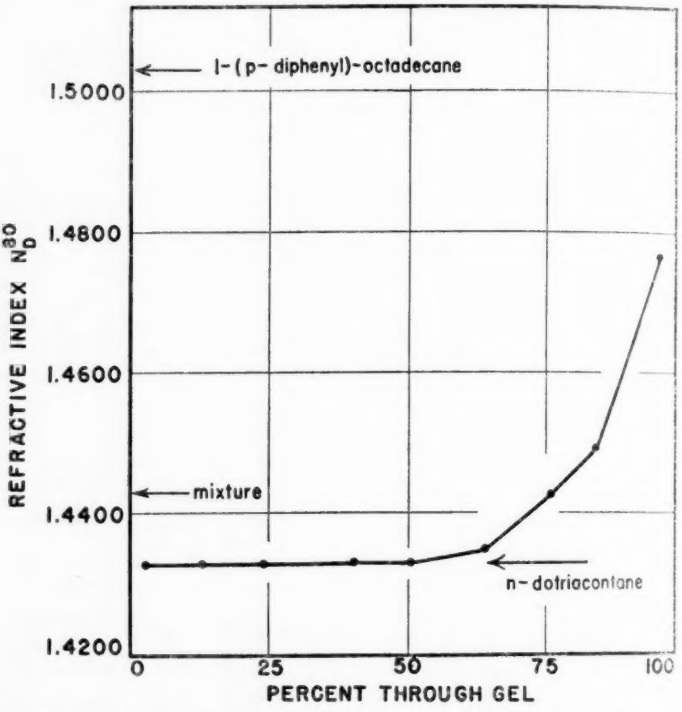


FIGURE 2.—*Plot showing the separation of a mixture of 23.85 g of n-dotriacontane and 4.72 g of 1-(p-diphenyl)-octadecane.*

The scale of ordinates gives the refractive index of the various fractions of the filtrate, and the scale of abscissas gives the percentage of material passed through the gel.

phenyl)-octadecane which contains 2 aromatic rings. It will be noted that a small amount (0.62 g) of material was obtained with a lower refractive index than that of the original 5-(7-tetrahydronaphthyl)-docosane. This small amount of material with lower refractive index was obtained because the 5-(7-tetrahydronaphthyl)-docosane, as already pointed out, was itself slightly fractionated on passage through gel. The remaining fractions show some separation of the compound with 1 aromatic ring from that with 2 aromatic rings, though the separation was not as sharp as that of nonaromatic from aromatic

hydrocarbons. Only 0.8 g of 1-(*p*-diphenyl)-octadecane was preferentially adsorbed from the mixture by 20 g of gel.

In experiment 4 it was found that substantially no separation occurred when a 9-to-1 mixture of the paraffin hydrocarbon, *n*-dotriacontane, with 5-(2-decahydronaphthyl)-docosane, which contains 2 naphthene rings (condensed), was filtered through silica gel under the same conditions as in the other experiments.

The author is grateful to B. J. Mair and F. D. Rossini for their suggestions and guidance, and to M. M. Haring, of the University of Maryland, for his interest in the problem.

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WASHINGTON, January 9, 1939.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1186

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RELATION BETWEEN MOISTURE CONTENT AND FLOW-POINT PRESSURE OF PLASTIC CLAY

By Ray T. Stull and Paul V. Johnson

ABSTRACT

A study was made to determine the relation between moisture content and "flow-point pressure" of a Maryland clay, a Georgia kaolin, and a Kentucky ball clay. Their moisture contents ranged from 17 to 34, 24 to 40, and 26 to 52 percent, respectively, and the flow-point pressures ranged from 8 to 400 lb/in^2. The clays were extruded from a knife-edged die by means of a cylinder and a mechanically driven piston. The flow-point pressures were determined on the average of 18 load readings for each test, and the percentages of moisture determined on a composite sample of 18 portions of the clay column. Tests were also made with two extrusion cylinders of different sizes and three dies of different diameters in a study of the effect of different cylinder and die sizes upon the flow-point load.

CONTENTS

	Page
I. Introduction	329
II. Clays included and scope of the investigation	330
III. Equipment and test methods	330
1. Extrusion apparatus	330
2. Preparation of the clay	331
3. Test procedure	331
IV. Results	332
1. Effect of variable die and extrusion cylinder sizes and distance of the piston head from the die on the flow-point load	332
2. Relation between flow-point pressure and moisture content	334
3. Comparative moisture contents of the clays at the same flow-point pressures	335
4. Flow-point pressures for soft- and stiff-mud consistencies	336
V. Conclusions	336

I. INTRODUCTION

When pressure is applied to plastic clay in the mold or die to form a product of uniform structure, the moisture content and the applied pressure must be adjusted so that the transmitted pressures within the clay will cause it to flow and fill the mold or die completely.

Considerable work has been done concerning the application of pressure to clays of different moisture contents in connection with studies of plasticity, and on the effect of molding pressure upon the physical properties of the dry and kiln-fired products. However, very little work has been done and information is meager concerning the relation between moisture content of clay and the corresponding pressure required to produce flow.

Bleininger and Ross [1] investigated a number of clays to determine the flow pressures required for different moisture contents. The clays

[1] *The flow of clay under pressure*, Trans. Am. Ceram. Soc. **16**, 392 (1914).

were extruded from a cylinder through a circular knife-edged orifice by means of a hand-operated testing machine and the load readings noted when movement of the clay at the orifice was observed. Moisture contents of the clay were plotted against corresponding flow pressures and their conclusion was that "The curves themselves are hyperbolic in character, as is to be expected." However, no equation was given to express the relation between moisture content and flow pressure.

MacGee, White, and Klinefelter [2] determined the flow pressures of a number of clays and shales with different moisture contents in a study of the effect of fine grinding on the flow pressure. Although no mention was made of the nature of the curves they obtained by plotting flow pressures against moisture contents, they are apparently hyperbolic in character.

In a previous investigation [3] over 300 determinations were made of the moisture contents and corresponding flow pressures of a Maryland clay. After the data had served their purpose, they were plotted, and the curve obtained indicated that the relation was hyperbolic in character, which is in agreement with the conclusion of Bleininger and Ross.[4] Inasmuch as the moisture content of the clay ranged only from 24 to 26 percent by weight of the dry clay, the data lacked sufficient spread for development of the equation for the curve and a new investigation was, therefore, undertaken in which the water content of the clay was varied over a range such that the clay was too soft at one extreme and too stiff at the other for practical molding purposes. Data were also obtained with different sizes of extrusion cylinders and dies to obtain an indication of their effect upon the nature and magnitude of "flow-point load." [5]

II. CLAYS INCLUDED AND SCOPE OF THE INVESTIGATION

Three clays representing a wide range in plasticity were included in the investigation. These were a Maryland clay, a Georgia kaolin, and a Kentucky ball clay. The moisture content of the Maryland clay was varied from 17 to 34 percent by weight of the dry clay. For the kaolin the range was from 24 to 40 percent and for the ball clay from 26 to 52 percent. The flow-point pressures ranged from approximately 8 to 400 lb/in.^{2}

III. EQUIPMENT AND TEST METHODS

1. EXTRUSION APPARATUS

The clay in the moist condition was placed in a cylinder provided with a die and piston, and pressure to produce extrusion of the clay was applied by means of a motor-driven screw-power beam-and-poise testing machine of 2,000-pounds capacity, the assembly for a test being shown in figure 1.

The extrusion cylinder (shown in fig. 2) used in obtaining the flow-point pressures was fitted with a piston having an area of 4 in.^{2} attached to a push rod. The exit end of the cylinder was provided

[2] *Properties of some Ohio red-firing clays*, J. Am. Ceram. Soc. **18**, No. 5, 158 (1935).
[3] Paul V. Johnson and R. T. Stull, *Performance of a hollow-ware extrusion machine with different combinations of augers, spacers, and dies*, J. Research NBS **14**, 711 (1935) RP798.
[4] See footnote 1, p. 329.
[5] See p. 332 for definitions of "flow-point load" and "flow-point pressure."

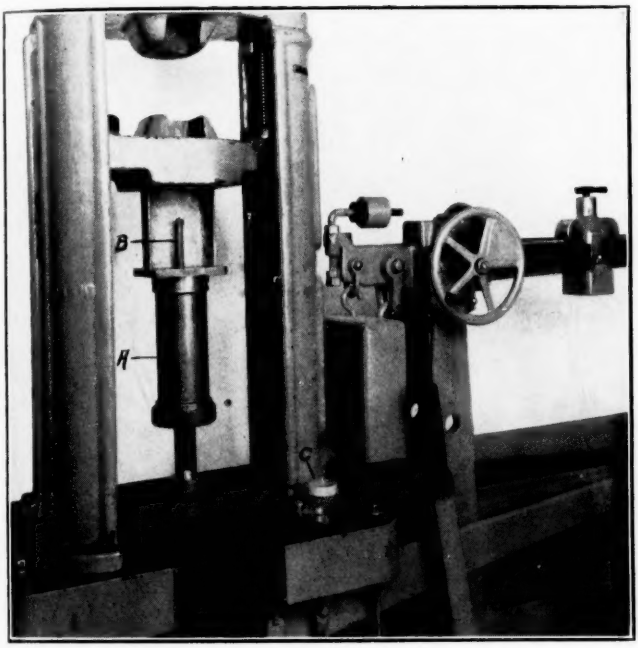

FIGURE 1.—*Machine used for determining flow-point pressures.*

A, Extrusion cylinder; *B*, clay column; and *C*, weighing bottle.

with a removable head containing the die, which consisted of a hardened tool-steel knife-edged orifice of ½-in. diameter.

Two extrusion cylinders and three dies, all of different dimensions, were used for determination of the effects of their variable sizes upon the flow-point load. The cylinders were 1½- and 2$^{9}/_{32}$-in. inside diameter, respectively, and the dies were ¼, ⅜, and ½ in. in diameter. Thus, six different combinations of cylinder and die were available.

2. PREPARATION OF THE CLAY

In preparing clay specimens of varying water content, a batch of 20 pounds of clay with sufficient water added to form a soft mass was kneaded for 2 hours in a closed pug mill and allowed to stand in the mill overnight. The following morning the cover was removed and the pug mill operated slowly and continuously while evaporation of moisture proceeded at room temperature.

Before the first clay sample was taken, the mill was allowed to operate for about 10 minutes to redistribute any moisture which may have evaporated and recondensed in the mill during the night, and also to overcome the "thixotropic" stiffening of the clay.

A portion of the clay was removed for each successive test at regular intervals as evaporation progressed, so that data were obtained for small differences in moisture content over the range from a very soft to a very stiff condition of the clay.

3. TEST PROCEDURE

The clay was transferred from the pug mill to the extrusion cylinder in small portions, each being thoroughly tamped until the cylinder was full. The clay was then made level with the top of the cylinder, and the die attached. The cylinder with its charge of clay was immediately placed in the testing machine with the die exit upward. The push rod and piston remained stationary and the movable head of the testing machine carried the cylinder downward at a rate of 0.7 in./min.

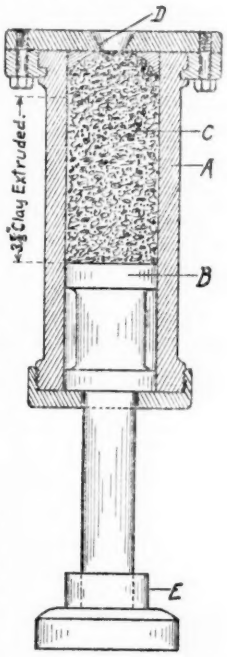

FIGURE 2.—*Sectional view of extrusion cylinder.*

A, barrel; *B*, piston, 4-in.² head; *C*, charge of moist clay; *D*, knife-edged die, ½-in. diameter, and *E*, rubber ring-pad.

In starting the extrusion mechanism from rest, the load would build up until movement of the clay through the die began. As the constant rate of piston displacement continued, the rate of extrusion of the clay increased with the load until both became fairly stable.

When about 4 to 5 in. of the clay column had issued, the testing machine was stopped and in approximately 3 to 5 seconds the clay column had virtually ceased flowing, and the load reading was immediately taken. The load required to start or to maintain extrusion is higher and less consistent than the load observed as the rate of extrusion approaches zero after stopping the testing machine. There-

fore, the load obtained under the latter condition was adopted in this investigation and is called "flow-point load," and the pressure in pounds per square inch of piston head is called "flow-point pressure."

For determination of the moisture content, a section of the freshly extruded clay column about ½ in. long was taken next to the die and placed in a weighing bottle. The procedure of taking a load reading and a corresponding portion of the clay column for the moisture determination was repeated 18 times over a piston travel of 3⅞ in., thus leaving about 1⅛ in. of clay in the cylinder. Each flow-point pressure was, therefore, obtained from the average of 18 load readings and the moisture content from a composite sample of 18 corresponding portions of the clay column.

IV. RESULTS

1. EFFECT OF VARIABLE DIE AND EXTRUSION CYLINDER SIZES AND DISTANCE OF THE PISTON HEAD FROM THE DIE ON THE FLOW-POINT LOAD

The 18 load readings observed during a test showed considerable variation, the reason for which was not at first apparent, inasmuch as the load readings could be made within an accuracy of ±1 percent. Table 1 shows typical variations in load readings for three tests taken at random, one for each clay. The reason for this variation in the consecutive load readings became apparent when data were obtained in an investigation of the effect on the flow-point load of variable die and extrusion cylinder sizes and distance of the piston head from the die when the load reading was observed.

TABLE 1.—*Maximum, minimum, difference, and average of load readings of a test taken at random for each clay*

Load	Clays and flow-point loads		
	Maryland clay (test 23)	Georgia kaolin (test 108)	Kentucky ball clay (test 68)
	Pounds	*Pounds*	*Pounds*
Maximum	444	322	36
Minimum	360	244	33
Difference	84	78	7
Average	391	287	33

In figure 3 the flow-point loads are plotted against corresponding distances of the piston head from the die when the load readings were taken for six tests made with the Maryland clay, in which the moisture content was maintained substantially constant. The plots indicate that the loads decrease in a "wave-like" manner as the piston moves toward the die; in general, suggestive of "sine waves" with reference to sloping axes. The relation of change in the slope of the axis to change in the size of the die was not established, but it does not appear to be a simple linear relation.

The wave-like changes in load produce an oscillation frequency of slightly more than 1 cycle for the length of piston displacement between the first and eighteenth load readings. This wave-like variation in load is also observed when clays are extruded at a constant

rate of flow by means of a piston, cylinder, and die, when the load readings are observed at regular time intervals.[6]

The results plotted in figure 3 indicate that the magnitude of the flow-point load is influenced by the size of extrusion cylinder, size of die, and distance of the piston head from the die when the load read-

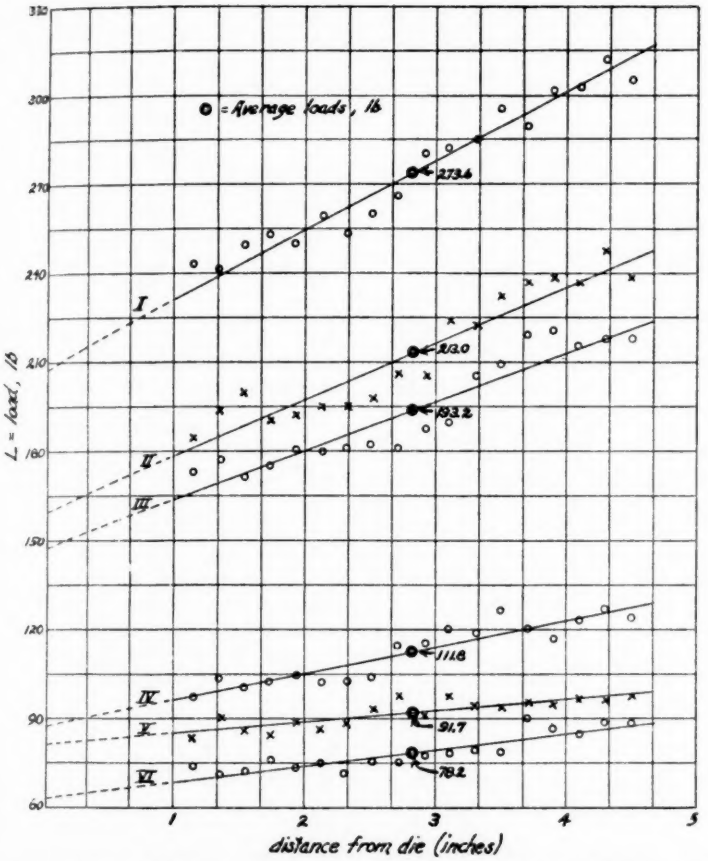

FIGURE 3.—*Effect of different extrusion cylinder and die sizes and distance of the piston head from the die upon flow-point load.*

Curves I, II, and III, extrusion cylinder, 2$\frac{9}{32}$ in. in diameter with ¼-, $\frac{3}{16}$-, and ⅛-in.-diameter dies, respectively.
Curves IV, V, and VI, extrusion cylinder, 1½ in. in diameter with ¼-, $\frac{3}{16}$-, and ⅛-in.-diameter dies, respectively.

ing is observed. In general, the load decreases with (a) decrease in diameter of the extrusion cylinder, (b) increase in diameter of the die, and (c) decrease in distance of the piston head from the die. Test results are, therefore, only comparable when using a definite equipment under a definite set of experimental conditions.

[6] R. T. Stull, *Wear of dies for extruding plastic clay*, BS J. Research **12**, 501 (1934) RP675. See p. 509 and fig. 5.

2. RELATION BETWEEN FLOW-POINT PRESSURE AND MOISTURE CONTENT

In the tests for the determination of the relation between moisture content and flow-point pressure of the clays, the pressures were obtained with the same cylinder of 4-in.^{2} cross-sectional area and die of

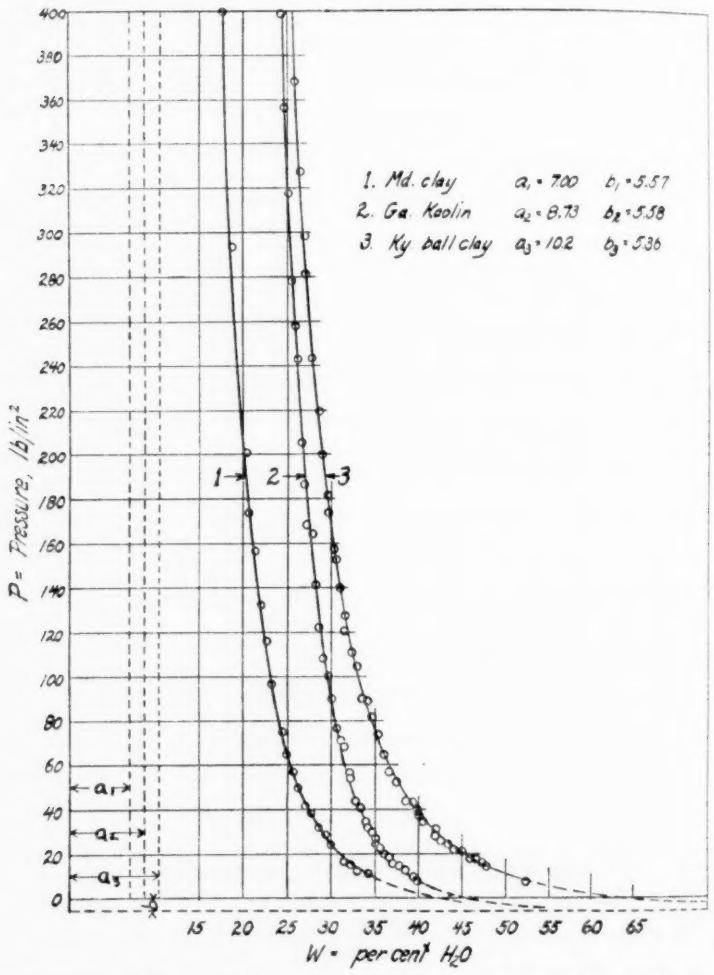

FIGURE 4.—*Relation between flow-point pressure (lb/in.^{2}) of piston head and moisture content of the clays, in percent, of the dry weight of the clay.*

½-in. diameter operated under the same experimental conditions; hence the results are comparable among themselves.

The curves obtained by plotting the average flow-point pressures against corresponding moisture contents of the clays are shown in figure 4. They are hyperbolic in character and, according to the experi-

mental system employed, the data indicate that the relation is of the form:

$$(p+b)(w-a)^m=K, \text{ or } p=\frac{K}{(w-a)^m}-b \quad (1)$$

in which

w = moisture content in percent of the dry weight of the clay
p = flow-point pressure in lb/in^2., of piston head, and
a, b, m, and K = constants.

TABLE 2.—*Values of the constants of equations 1 and 2*

Clay	a	b	m	K	Moisture content [1] when $p=0$
Maryland clay	7.00	5.57	3.50	174×10^4	44.15
Georgia kaolin	8.73	5.58	4.95	341×10^4	46.24
Kentucky ball clay	10.20	5.36	3.37	411×10^4	65.95

Average of b values=5.50, approximately

[1] In percent of dry weight of clay.

Comparison of the values of the constants determined for the clays studied may be seen in table 2.

Although the extrapolation of the curves outside of the region covered by the data may not be justifiable, it is helpful in understanding the significance of the constants obtained from the data. The value of asymptote a indicates the content of moisture with which the hard dry clay must be imbued before it becomes amenable to flow (theoretically) at infinite pressure.

When $p=0$, then

$$w=\left(\frac{K}{b}\right)^{1/m}+a \quad (2)$$

in which w represents the percentage of moisture content of the clay at which it would flow (theoretically) under the slightest pressure.

The values for a, m, and K although constant for a definite clay, are different for different clays, and b is evidently constant for all three clays. The values of b obtained experimentally for the Maryland clay and the Georgia kaolin are substantially the same, whereas it is slightly less for the Kentucky ball clay. The average value of b, however, is approximately 5.50.

At moisture contents of the clay near the value w (eq 2), a decrease of 1 percent in moisture causes only a slight increase in the flow-point pressure, but when the moisture content approaches the value of a, a very small decrease in moisture causes an enormous increase in the flow-point pressure.

3. COMPARATIVE MOISTURE CONTENTS OF THE CLAYS AT THE SAME FLOW-POINT PRESSURES

It is well known that plastic clays highly colloidal in nature require more moisture than the less plastic clays for proper workability. This

relation may be seen by comparison of the moisture contents of the three clays at the same flow-point pressures. In table 3 are given the moisture contents of the clays at flow-point pressures of 10 and 200 lb/in². The difference of 190 lb in flow-point pressure (between 10 and 200 lb) results from a difference in moisture content of 14.45 percent for the Maryland clay, 12.34 percent for the Georgia kaolin, and 21.53 percent for the Kentucky ball clay.

TABLE 3.—*Moisture contents of dry weight of the clays at two different flow-point pressures*

Clays	Moisture content at 10 lb/in²	Moisture content at 200 lb/in²
	Percent	*Percent*
Maryland clay	34.70	20.25
Georgia kaolin	39.13	26.79
Kentucky ball clay	50.71	29.18

4. FLOW-POINT PRESSURES FOR SOFT- AND STIFF-MUD CONSISTENCIES

The method most generally employed in both factory and laboratory for judging the desired consistency of a clay for molding, is by appearance, feel, and behavior in molding. Using this method for judging the proper consistencies for the equipment used, it appears that the so-called soft-mud condition of the clays was obtained at a flow-point pressure of approximately 20 lb/in². and the stiff-mud condition at about 80 lb/in².

A difference of 1 percent in moisture content at the soft-mud condition causes a difference in flow-point pressure of approximately 4 lb/in²., while the pressure difference at the stiff-mud condition is about 22 lb/in². for a difference of 1 percent of moisture.

V. CONCLUSIONS

From the data obtained under the experimental conditions herein described, the following conclusions seem justifiable:

1. The flow-point load decreased with decrease in diameter of extrusion cylinder, with increase in diameter of die, and with decrease in distance of the piston head from the die.

2. The plot of the flow-point load against corresponding distance of the piston head from the die when the load reading is observed produced a curve similar to a "sine wave" with reference to a sloping axis.

3. The relation between flow-point pressure and percentage of moisture content of the clays can be expressed by the equation $(p+b)\ (w-a)^m=K$,
where

p=flow-point pressure in lb/in². of piston head
w=moisture content of the clay in percent of the dry weight of the clay, and
a, b, m, and K=constants.

The values of a, m, and K were constant for a definite clay but different for different clays, while asymptote b was substantially constant for all three clays. The asymptote a represents the per-

centage of uniformly distributed moisture in the clay before it becomes amenable to flow at theoretically infinite pressure.

4. When $p=0$,

$$w=\left(\frac{K}{b}\right)^{1/m}+a,$$

in which w represents the percentage of moisture of the clay at the transition point where, theoretically, the slightest pressure would cause flow.

5. The soft-mud consistency of the clays was obtained at a flow-point pressure of about 20 lb/in^2., and the stiff-mud consistency at approximately 80 lb/in^2. A difference in moisture content of 1 percent for the soft-mud consistency caused a difference of approximately 4 lb/in^2. in flow-point pressure, and a like difference in moisture for the stiff-mud consistency caused a difference of approximately 22 lb/in^2. in flow-point pressure.

WASHINGTON, January 16, 1939.

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EFFECT OF THE SOLUBILITY[1] OF GLASS ON THE BEHAVIOR OF THE GLASS ELECTRODE

By Donald Hubbard, Edgar H. Hamilton, and Alfred N. Finn

ABSTRACT

Application of an interferometer method previously used for determining the relative solubility of optical glasses, to a glass which is commonly used for making glass electrodes, gave results leading to the following conclusions:

1. The solubility increases rapidly as the pH of most solutions increases above 8.5 or 9.
2. At all values below pH 7 for the solutions investigated (except 10 N H_2SO_4) this glass exhibits a slight swelling.
3. The rate of swelling is repressed in the acid region beyond pH 2.
4. At intermediate pH values 3.1 to 4.0 the rate of swelling is repressed by high concentrations of magnesium sulfate.

Considering these conclusions in connection with the performance of glass electrodes, these regions of marked solubility change correspond to the regions of pronounced voltage departures exhibited by electrodes made from this glass. That the anomalies of the glass electrode are definitely associated with the solubility of the glass has been further demonstrated both by the use of glasses which do not exhibit swelling in the acid range, (and hence no detectable change of swelling in the "super-acid region"), and by measurements made in alkaline solutions, such as aqueous ammonia, in which soluble silicates are not formed. Under these circumstances the voltage departures are greatly decreased or completely eliminated.

For every case investigated, voltage departures of the glass electrode have been found to be accompanied by changes in the solubility of the glass.

CONTENTS

	Page
I. Introduction	339
II. Experimental procedure	340
III. Data and results	340
IV. Conclusions	348
V. References	348

I. INTRODUCTION

The voltage of the glass electrode follows approximately the straight-line relation of the Nernst equation over an extended range of hydrogen ion concentrations. However, in most solutions a marked voltage departure begins at a pH of 8.5 or 9 and becomes greater with increased alkalinity. In the extreme acid range another voltage departure appears [1] [2] in a direction opposite to that in the alkaline region. Other voltage departures occur in salt solutions of high concentration and in ethanol solutions [2]. Since such anomalies in the voltage of any electrode suggest changes in the nature of the equilib-

[1] The term "solubility" is not used in this report in a strict sense and is not to be confused with any physicochemical interpretation of the word.

[2] Figures in brackets indicate the literature references at the end of this paper.

rium between the material of the electrode and its environment, a study of the solubility of the glass commonly used in electrode manufacture [3] was undertaken, employing the interferometer method previously used for estimating the rate of solution of optical glasses and comparing durability test methods [4, 5].

II. EXPERIMENTAL PROCEDURE

The interferometer method was used because it offered a rapid and convenient means of making a semiquantitative study of the relative rates of solution of the glass over an extended range of temperature and pH. Rectangular specimens (approximately 2 by 3 cm) of the glass, with surfaces sufficiently flat to show interference bands when placed under a fused-quartz optical flat, were partially immersed in the desired solution, the surface of which was covered throughout the period of test with a thin layer of liquid petrolatum to prevent evaporation. The desired temperature was maintained constant to $\pm 0.1°C$ by means of an electrically heated thermostated water bath. Under these conditions very satisfactory and uniform attack of the immersed surface was obtained, beginning at the oil-solution interface. The magnitude of the attack was readily ascertained with a Pulfrich viewing apparatus, using an unfiltered helium light for illuminating the interferometer. Some determinations were made in white light without the use of the viewing apparatus, because this procedure offered an easy and rapid means of ascertaining if the exposed surface of the specimen had undergone swelling or had dissolved during the test.

All emf measurements were made with a Leeds & Northrup portable potentiometer-electrometer. Although the emf measurements of the solutions were made at room temperature, while the solubility experiments were made in most cases at higher temperatures, no account was taken of the small shift in pH of the buffer which accompanied this temperature change [6, 7]. Since all electrode measurements were made in Pyrex beakers, the solubility tests were also carried out in similar vessels, even though Pyrex is known to be attacked by the alkaline solutions [8, 9]. In no case did the pH of the buffer solutions shift as much as 0.1 from this cause, during the period of any test.

III. DATA AND RESULTS

The data plotted in figure 1 show the attack[3]-pH curve on Corning 015 glass by Britton universal buffer mixtures [10] over the range pH 2 to 12 for 6 hours at 80° C. At and below pH 7 the glass exhibits a slight uniform swelling, which, for convenience, is plotted as negative attack. Near pH 8 the solubility approaches zero and thereafter increases rapidly with increasing alkalinity. The region between pH 8 and 9 corresponds to the region in which voltage departures of the glass electrode just become noticeable, and as the pH increases above 9 the voltage departure increases rapidly, as does the solubility. For the pH region in which the transition from "negative" to positive attack occurs, excessive positive attack at the oil-solution interface was obtained, while below, in the main body of the solution, little or no attack was observed. For the specimen at pH 7 a marked positive

[3] The term "attack" is used to express the thickness in fringes of the layer of glass removed under the conditions of the experiment. One fringe corresponds to approximately 0.29 micron.

attack appeared at the interface while swelling was exhibited below. A possible explanation for this may lie in the orientation of ions at the oil-solution interface [11, 12, 13] resulting in an increased alkalinity there. To account for the surface cuts observed, the pH at the interface would necessarily be greater than 9.

The voltage departure of the glass electrode in the alkaline region increases rapidly with increased temperature [14], and from the data plotted in figure 2 it is shown that the rate of solution of the glass approximately doubles for each 10° C rise in temperature.

That the voltage departures of the glass electrode are associated with the solubility of the glass is indicated by its behavior in aqueous-ammonia solutions in the absence of sodium ions [15] and is illustrated

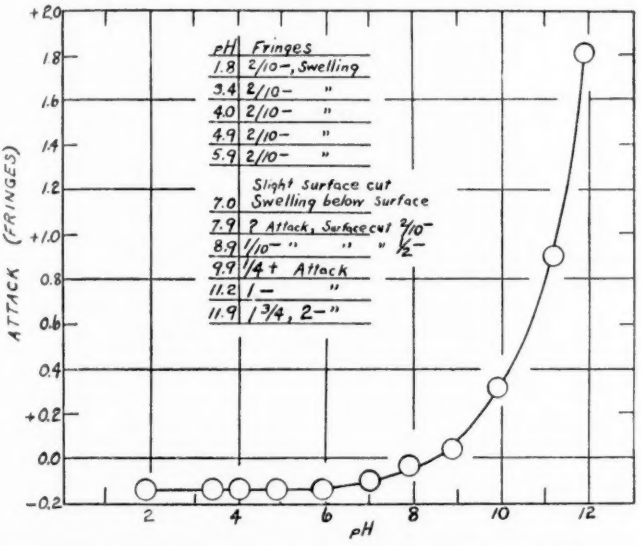

FIGURE 1.—*Attack-pH curve of Corning 015 glass, exposed 6 hours at 80° C to Britton universal buffer mixtures covering the range* pH *2 to 12.*

The plotting of the data in this and succeeding figures is not intended to convey the idea that the attack values were determined within close limits. The size of the circles does not represent the probable error of the data presented, but merely indicates that exactness is not implied. The data, however, are known to be sufficiently reliable to justify the trends indicated by the curves.

by the data in figure 3. The interesting feature of this voltage-pH curve for ammonia buffers is that it continues as a straight line until the pH of full-strength ammonia solution is approached, at which point the voltage departs in a direction opposite to that normally encountered in alkaline solutions. This suggests that the glass is attacked less by ammonia solution at pH 13.3 than by lower concentrations, such as pH 12.5. Solubility tests in ammonia solutions at those pH values for 15 days at room temperature confirmed this, since the one at pH 12.5 produced an attack of ¼ fringe, while the effect of the other at pH 13.3 was hardly detectable (plotted as circles, fig. 3). Comparing the voltage-pH curve for the ammonia buffer with that for the universal buffer (plotted +, fig. 3), one would expect to find the glass more resistant to attack of the NH_4^+ than of the Na^+ of the universal buffer at the same pH. This was also found

to be true. Solubility tests for 18 hours at 50° C showed an attack by the NH_3 solution at pH 12.4 to be less than 2/10 fringe, while that by the universal buffer at the same pH was greater than 1/2 fringe (plotted × in fig. 3). From these results it seems probable that variations in magnitude of the voltage departure for different cations [1] in the alkaline range are primarily a question of differences in rate of solution of the glass in the presence of these ions. However, additional quantitative data must be obtained before such a conclusion can be substantiated.

Concerning the voltage departure in the "super-acid" region, figure 4 shows the effect produced on Corning 015 glass by hydrochloric

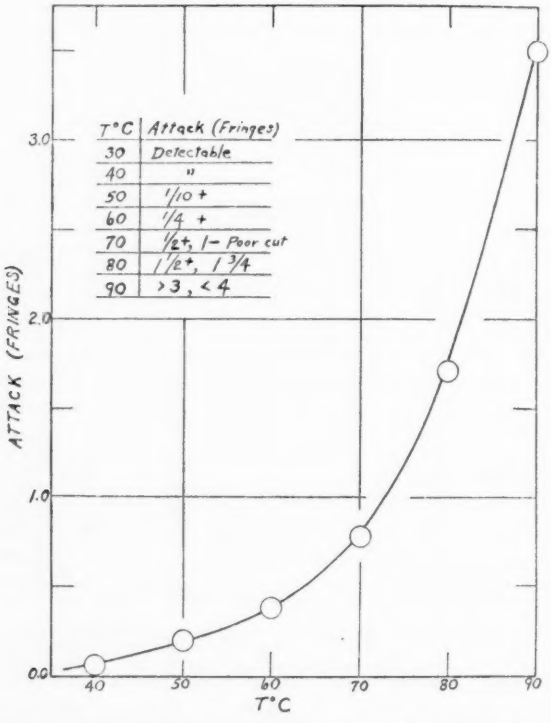

FIGURE 2.—*Temperature effect on rate of solution of Corning 015 glass in 5-percent NaOH for 3 hours at 80° C.*

sulfuric, and phosphoric acids. As the acidity increases the amount of swelling in 48 hours at 80° C. is repressed. Similar voltage departures are reported for high concentrations of other acids [16] and, although the solubility tests have not been made, one can predict with reasonable certainty from Donnan membrane considerations and the distribution law that repression of swelling will be exhibited in these cases also. Although the specimens exhibit less swelling in the high concentrations, it must be borne in mind that this diminished effect can be attributed to repression of the swelling of the gelatinous silica layer resulting from the change in osmosis, caused by increased

concentration of electrolyte, or to a partial solution of that silica, or to a combination of both.

TABLE 1.—*Voltages for glass electrodes prepared from three commercial glasses, with reference to the saturated calomel half-cell*

pH of solutions with H_2 electrode	Emf of the glass electrodes		
	Glass *A*	Glass *B*	Glass *C*
	HCl		
	Volts	*Volts*	*Volts*
2.85	−0.265	−0.157	−0.272
1.93	−.317	−.207	−.323
1.00	−.368	−.257	−.375
0.0	−.427	−.315	−.438
−1.01	−.487	−.369	−.498
	H_2SO_4		
2.70	−0.270	−0.165	−0.282
1.93	−.317	−.206	−.328
1.10	−.363	−.254	−.374
0.06	−.425	−.308	.....
−1.11	−.492	−.378	−.505
	H_3PO_4		
3.20	.....	−0.146	−0.255
2.39	−0.290	−.180	−.300
1.78	−.325	−.214	−.334
1.06	−.365	−.252	−.376
−0.01	−.429	−.315	−.441

At pH values below 7 the universal buffer produced no detectable effect on the glass in 6 hours at 80° C. Aqueous solutions of HCl, H_2SO_4, and H_3PO_4 at pH values below 3 also produced no effect under similar conditions nor was there any detectable attack or swelling in 48 hours at 80° C.

Further evidence that the voltage departures are associated with changes in solubility of the glass is shown by the fact that electrodes prepared from glasses *A*, *B*, and *C* (table 1) exhibited no detectable swelling or voltage departures in the super-acid region. Typical attack-pH data and the corresponding emf-pH relation for glass *A*[4] are plotted in figure 5 as curves α and β, respectively. Below pH 3 the data plotted are for HCl, H_2SO_4, and H_3PO_4, while above this pH the data are for the universal buffer. Under the conditions of these determinations no voltage departure from the straight-line relation was indicated for the "super-acid" region. However, columns 2 and 3 (table 2) and figure 6 give the voltage departures from the hydrogen electrode of an electrode of Corning 015 and one of glass *A* in HCl solutions under more exacting conditions.

[4] See table:

Composition (approximate)	
	Percent
SiO_2	72.1
CaO	10.1
Na_2O	13.5
MgO	3.3
R_2O_3	0.7

TABLE 2.—*Electromotive force between the hydrogen electrode and glass electrodes prepared from glasses 015 and A, in* HCl *and* H_2SO_4 *solutions*

Normality of solutions (approximate)	Glass (HCl solution)		Glass (H_2SO_4 solution)	
	015	A	015	A
	Volts	*Volts*	*Volts*	*Volts*
0.001	0.218	0.193	0.215	0.191
0.01	.218	.193	.217	.191
0.1	.216	.194	.217	.192
1.0	.213	.194	.215	.192
5.0	.194	.192	------	------
10.0	.175	.184	.217	.192

For these determinations the glass electrodes were compared directly with the hydrogen electrode, and the concentration of the

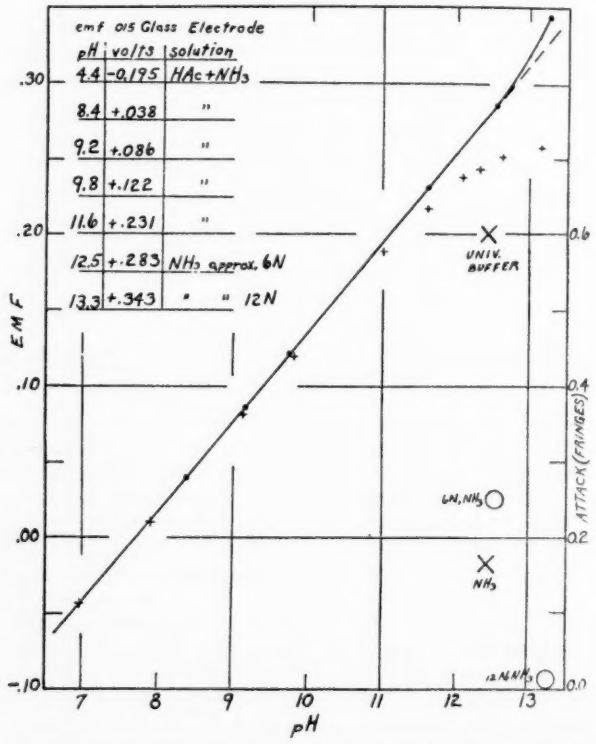

FIGURE 3.—*Comparison of the voltages of an electrode of Corning 015 glass in* $CH_3COOH+NH_3$ *solutions* (•) *and Britton universal buffer mixtures* (+), *with the solubility of the glass in these solutions.*

HCl was extended beyond pH −1.01 (approximately 5 *N*) used in the previous case. These departures are plotted against log 1/*N*

instead of pH in order to avoid the confusion of thought caused by activity coefficients for high concentrations of HCl, which indicate a degree of dissociation of 200 to 1,000 percent [17]. Although the data presented indicate that glass *A* has very desirable emf relations in the super-acid region, its resistance is so high it cannot be considered as more satisfactory than Corning 015 glass.

Since voltage departures in the super-acid region have become of theoretical concern, it is of interest to note that we have repeatedly blown electrodes of Corning 015 glass which have exhibited no definite voltage departure in H_2SO_4 solutions, while doing so in HCl. Typical data illustrating this statement are given in table 2 (columns 2 and 4)

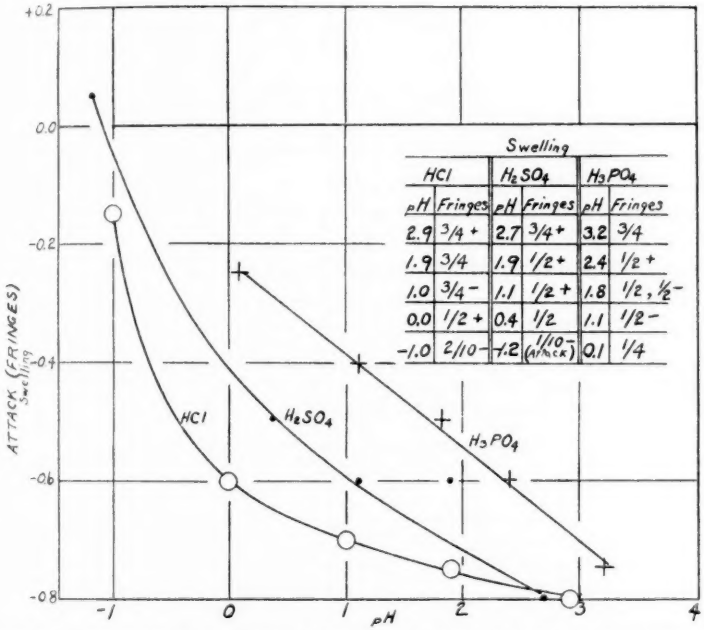

FIGURE 4.—*Repression of swelling of Corning 015 glass by increasing concentrations of* HCl (○), H_2SO_4 (•), and H_3PO_4 (+) *for 48 hours at 80° C.*

for an electrode prepared from 015 glass compared with the hydrogen electrode. Although it cannot be demonstrated, we feel this is caused by differences in solubility of the particular sample of glass under observation in these solutions. Such irregularities in the voltage departures of the glass electrode in the acid region are confusing, and it was thought that the behavior of the glass electrode toward hydrofluoric acid solutions, which attack glass relatively rapidly, might throw some light on the subject.

Table 3 gives the voltage departures from the straight-line relation when the glass electrode was compared with the hydrogen electrode in HCl, H_2SO_4, and HF solutions of various concentrations. The voltages in HF are somewhat uncertain because of its vigorous action on the glass but, as expected, show large departures for the solutions of higher concentrations. Concentrations greater than one normal

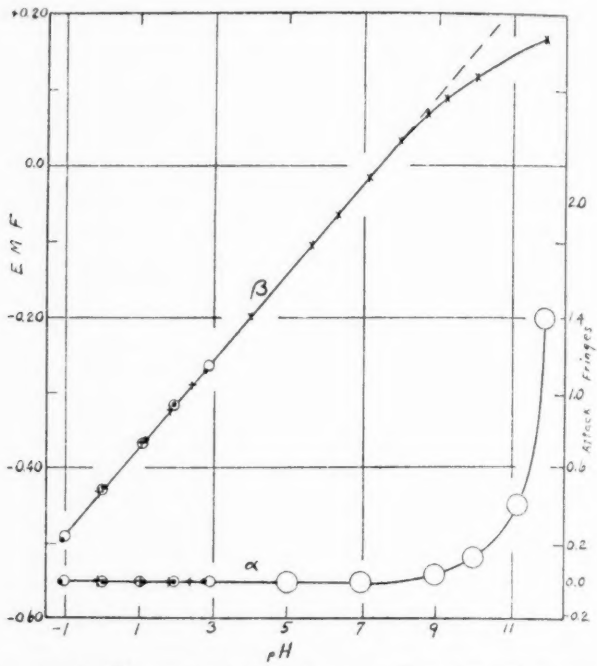

FIGURE 5.—*Attack*-pH *curve, typical for glasses A, B, and C* (◯) *of table 1, and the voltage*-pH *response of an electrode prepared from glass A in* HCl (○), H_2SO_4 (•), H_3PO_4 (+), *and Britton universal buffer* (×).

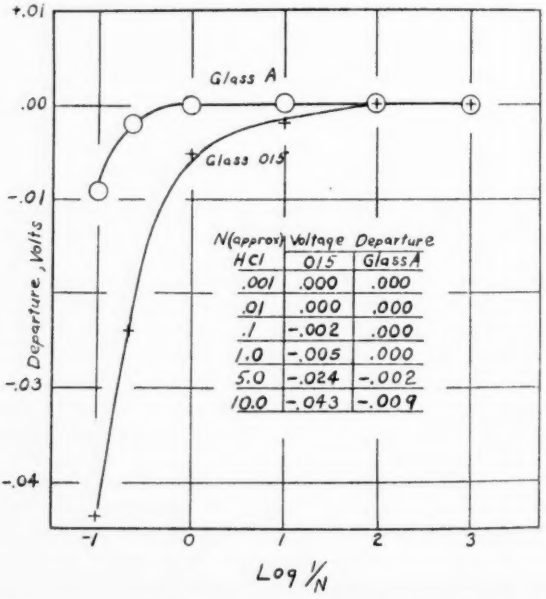

FIGURE 6.—*Voltage departures from the hydrogen electrode of electrodes prepared from glasses 015,* (+), *and A,* (◯), *in* HCl *solutions*

are not reported because the hydrofluoric acid destroyed the glass electrode.

Voltage departures similar in direction to that obtained in the super-acid region have been reported for concentrated salt solutions at intermediate pH values [2]. To determine if these departures are accompanied by repression of swelling, solubility tests in *M*/20 acid potassium phthalate solutions containing $MgSO_4$ were made. The data are plotted in figure 7 and indicate that a repression of swelling is produced by the higher concentrations of $MgSO_4$. If these data

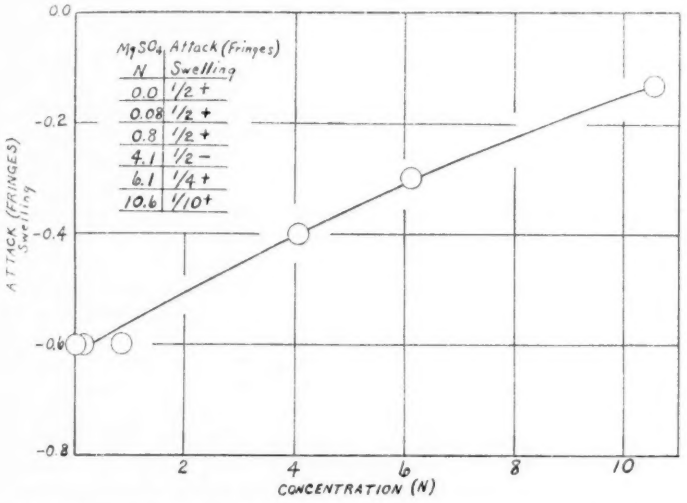

FIGURE 7.—*Repression of swelling of Corning 015 glass by* $MgSO_4$ *solutions buffered with M/20* KH *phthalate.*

were plotted on a pMg basis, a curve similar to the solubility-pH curves for the concentrated acid solutions would be obtained.

TABLE 3.—*Comparison of voltage departures of Corning 015 glass electrode in* H_2SO_4, HCl, *and* HF *solutions, the reference voltage being that obtained in M/20* KH *phthalate solution*

N (approx.)	H_2SO_4[1]	HCl[1]	HF
	Volts	*Volts*	*Volts*
0.001	0.092	0.000	0.003
.01	.000	.000	.015
.1	.000	.002	.054
1.0	.002	.005	.188
5.0	-------	.024	-------
10.0	.000	.043	-------

[1] Based on data in table 2 for 015 glass.

TABLE 4.—pH *of aqueous solutions of M/20 KH phthalate containing varying amounts of* $MgSO_4$

$MgSO_4.7H_2O$ per 100 ml of solution	pH
Grams	
0	4.0
1	3.9
10	3.6
50	3.2
75	3.1
5	[1] 6.2

[1] This solution contained no KH phthalate.

Although the pH of the solutions changed from 4.0 to 3.1 (see table 4) as the concentration of the $MgSO_4$ increased, it is evident from figure 1 that this pH change alone would not produce a detectable effect on the amount of swelling.

Another voltage departure of the glass electrode has been reported for solutions in which water is progressively replaced by ethanol [2], the departure being again in a direction similar to that reported for the super-acid region. Satisfactory solubility experiments were difficult to make in ethanol because of its volatility and also because the density of 95-percent C_2H_5OH is not sufficient to float the oil layer. However, it was possible to make some solubility comparisons between ethanol and water by adding equal quantities of H_2SO_4 to distilled water and to 95-percent C_2H_5OH until the density of the latter was raised sufficiently to float the oil layer. Results obtained in this manner at 70° C for 48 hours showed a swelling of less than 0.2 fringe for the water solution, while the effect on the glass by the ethanol solution was not definitely detectable.

Solubility comparisons in water-alcohol solutions buffered with *M*/20 KH phthalate were also attempted. Seven days at room temperature gave approximately 0.1-fringe swelling in the water solution, the 50-percent ethanol solution gave a detectable swelling, while 85- and 95-percent solutions gave no detectable effect. Although these experiments are not all that might be desired, we feel they are qualitatively correct.

IV. CONCLUSIONS

In all cases that have been studied voltage departures of the glass electrode have been found to be associated with marked changes in the solubility of the glass. This leads the authors to believe that the variations in magnitude of the voltage departures of the glass electrode in the presence of different ions are primarily caused by solubility differences of the glass produced by these ions and not by an equilibrative response of the electrode to ions other than hydrogen. From this and further investigations it may be possible to form a more satisfactory picture of the mechanism of the glass electrode and perhaps to extend its range of usefulness.

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RESEARCH PAPER RP1188

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ESTABLISHMENT OF A TEMPERATURE SCALE FOR THE CALIBRATION OF THERMOMETERS BETWEEN 14° AND 83° K

By Harold J. Hoge and Ferdinand G. Brickwedde

ABSTRACT

Seven resistance thermometers (six Pt; one 90Pt:10Rh alloy) have been calibrated on the thermodynamic scale by comparison with a helium gas thermometer. The boiling point of oxygen was taken to be 90.19° K, and computations were made in such a way as to secure continuity between the International Temperature Scale and the scale being established. On the latter scale the triple point of normal hydrogen was found to be 13.96° K and the boiling point 20.39° K. Tables have been prepared by means of which temperatures corresponding to observed resistances may be obtained by linear interpolation.

CONTENTS

		Page
I.	Introduction	351
II.	Apparatus	352
III.	Theory	355
IV.	Reduction to the thermodynamic scale	357
V.	Procedure and calculations	359
VI.	Data and results	362
VII.	Estimation of errors	371
VIII.	Comparison with previous work	372

I. INTRODUCTION

There are in the United States at the present time 13 laboratories equipped or being equipped to produce liquid hydrogen, liquid helium, or both, and the number is growing steadily. Many of the investigations being carried on in these laboratories require the precise measurement of temperatures in the region below 83° K (−190° C), and the National Bureau of Standards has received a number of requests for calibrations in this temperature range. The International Temperature Scale [1] defines no standard procedure for the measurement of temperatures below −190° C, and as a consequence it has been customary for cryogenic laboratories to calibrate their temperature-measuring instruments by direct comparison with a gas thermometer. The difficulties inherent in gas thermometry make it highly desirable that some simpler procedure be found, which may be used in all investigations where the measurement of temperature is not itself the primary object. Since from 660° C down to −190° C the International Temperature Scale is based on the resistance of platinum, a desirable solution of the problem would be to extend the useful range of the platinum resistance thermometer to lower temperatures. The

[1] George K. Burgess, BS J. Research **1**, 635 (1928) RP22.

provisional temperature scale described in this paper represents such an extension. Apparatus is now being set up to make this scale available to other laboratories by the calibration of thermometers which may be submitted for test. The purpose of this paper is to describe the establishment of this scale, which is to serve (1) as the basis for calibrations made by the National Bureau of Standards between 14° and 83° K and (2) as the scale to be used by this Bureau in reporting the results of its own investigations.

Since the National Bureau of Standards, in common with other standardizing laboratories, makes all calibrations above −190° C on the International Temperature Scale, it is important that the scale extending to lower temperatures should join smoothly with it at its lowest point. This continuity can be obtained by using the oxygen point as the primary fixed point in determining the constant of the gas thermometer, rather than the ice point, which is the more usual procedure, and by assigning to it the same temperature on both scales. The scale described in this paper is based on seven resistance thermometers (six Pt; one 90Pt:10Rh alloy) whose resistances have been determined as a function of temperature by comparison with the gas thermometer.

The resistances of these thermometers will be checked from time to time at the triple point and boiling point of hydrogen, at the boiling point of oxygen, and at the ice point. It is planned in subsequent investigations to determine a number of other fixed points on the scale described. With a sufficient number of such points established, the maintenance of the scale will not be dependent on the preservation of the seven original thermometers.

It is hoped that the scale will be found to be in agreement with the thermodynamic scale to within ±0.02°. When a program for thermometry was laid out it was considered advisable to establish first a provisional scale of reasonable accuracy without waiting for the construction of more elaborate apparatus with which somewhat greater accuracy might have been attained. The continuation of this program includes, however, the construction of a new and more accurate gas thermometer with which not only to improve the present provisional scale but also to determine fixed points throughout the region below the ice point.

II. APPARATUS

There was available the low temperature adiabatic calorimeter used by Southard [2] and his collaborators in their calorimetric investigations. This calorimeter had been used by Southard and Milner [3] as a cryostat for the gas thermometer with which they calibrated their resistance thermometers. After some changes, designed to improve its accuracy, this apparatus was used in the present work.

The thermometer bulb and cryostat are shown schematically in figure 1. Surrounding the heavy cylindrical copper bulb was a thermal shield with independent heaters in top, side, and bottom, and outside the shield in turn was a vacuum-tight brass container. Outside this container was a dewar flask which was filled with liquid hydrogen (in some cases with liquid air). This dewar flask was entirely enclosed by a metal jacket (not shown). By reducing the

[2] J. C. Southard and F. G. Brickwedde, J. Am. Chem. Soc. **55**, 4378 (1933).
[3] J. C. Southard and R. T. Milner, J. Am. Chem. Soc. **55**, 4384 (1933).

pressure inside this jacket with a vacuum pump, temperatures down to 55° K could be obtained with liquid air and temperatures down to

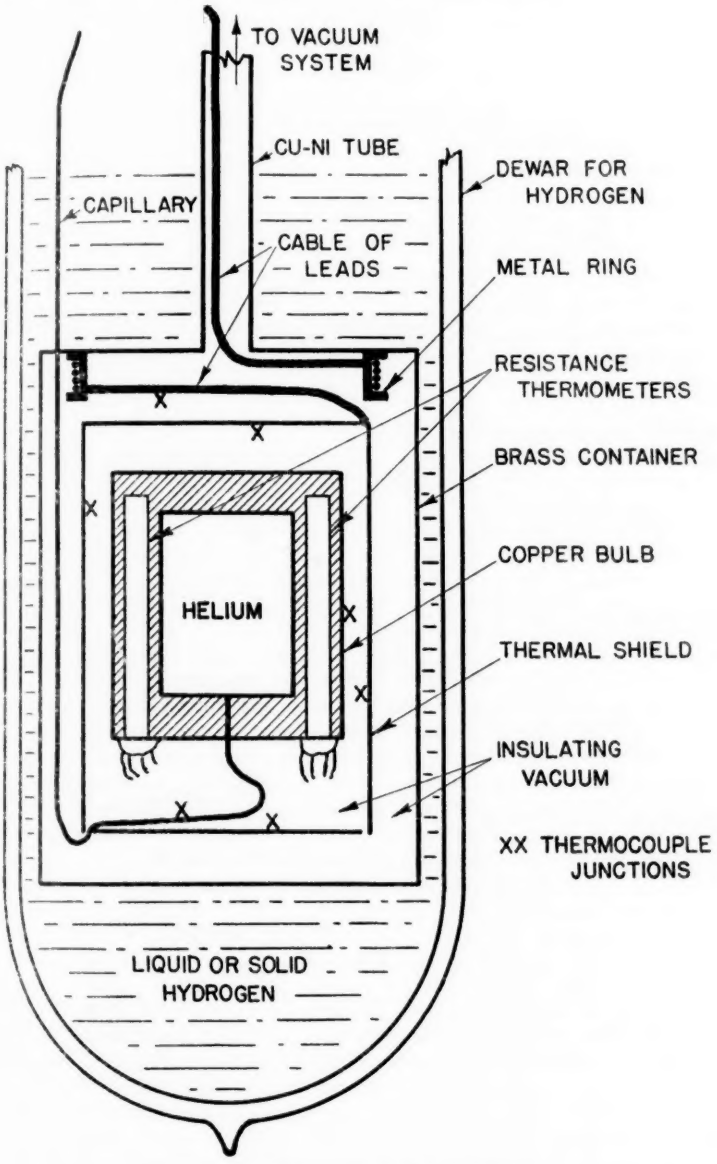

FIGURE 1.—*Thermometer bulb and cryostat.*

10.5° with (solid) hydrogen. The metal jacket was always surrounded by liquid air before filling the inner dewar with liquid hydrogen.

The copper-nickel capillary led to a mercury manometer where the pressures were read on a glass mirror scale. The end of the capillary passed through a turned-brass plug which was waxed into the short arm of the manometer. On the bottom of this plug was a sharp point to which the mercury was adjusted by means of a leveling reservoir before each reading. The long arm of the manometer was connected to a vacuum system and the mercury columns were thermally protected by light aluminum shields. Thermocouple junctions were placed at 10-cm intervals along the portion of the capillary extending from the brass container to the region at room temperature. The reference junction for these thermoelements was in melting ice. Six differential thermocouples (marked $\times$ in fig. 1), having a common junction on the bulb itself, indicated any temperature differences between the bulb and the points marked $\times$. It was necessary to furnish separate heaters both for the cable of leads and for the capillary. The input to the various heating circuits was regulated to keep the indications of the differential thermocouples as near zero as possible. Under these conditions the bulb could be kept at constant temperature as long as desired.

All of the resistance thermometers used were of the four-lead coiled-helix type wound on mica crosses, as described by Meyers,[4] but were sealed into cylindrical platinum cases (5 by 50 mm), filled with helium to promote rapid attainment of thermal equilibrium. The leads were brought out through a glass seal at the end of each case. Two resistance thermometers are shown in place in figure 1. Low-melting solder was used to insure good thermal contact between the thermometer cases and the copper block. All of the thermometers had been repeatedly annealed at approximately 500° C until heating to the sulfur point (444.6° C) did not change their ice-point resistances by more than the equivalent of 0.001°. No great difficulty was experienced in making thermometers which fulfilled this requirement. However, the 7 thermometers chosen were the best of a group of 12, not all of which satisfied the condition just laid down. The ice points of the seven thermometers have been checked several times during the progress of the investigation, some of them over a period of nearly 3 years, and no significant trend has been detected. The constants of the thermometers used are given in table 4, page 362.

The leads from the thermometers were wrapped several times around the bulb and shellacked down, so as to minimize heat leaks to the thermometers. The leads passed from the bulb to a groove in the radiation shield, passed several times around it, and emerged from the top of the shield, where all the leads were collected into a cable and wound with a heater. After making several turns around a metal ring, the cable passed up through the central copper-nickel tube and emerged from the vacuum system through a wax joint at room temperature. The purpose of the metal ring, which was soldered to the top of the brass container, was to cool the leads to the temperature of the refrigerating bath. The central copper-nickel tube led to a vacuum system into which helium could be admitted whenever the gas thermometer was to be brought rapidly to the temperature of the bath. This vacuum system was entirely independent of the one to which the manometer was connected.

[4] C. H. Meyers, BS J. Research **9**, 807 (1932) RP 508.

Resistances were measured on a thermostated Wheatstone bridge of the type designed by Mueller.[5] The thermocouples on the capillary were read with a potentiometer; those on the temperature-controlling system were arranged for direct connection to a galvanometer.

III. THEORY

A real gas, confined in a volume which is strictly constant and at uniform temperature throughout, exerts a pressure which is a single-valued function of the temperature. This pressure may be used to define a scale of temperatures according to the equation

$$p = cT_g, \qquad (V \text{ const}), \qquad (1)$$

where the subscript g indicates that the scale depends on the kind of gas and on its density, and does not necessarily agree with the thermodynamic scale. The constant c is fixed by the condition that T_g increase by 100° in passing from the ice point to the steam point.

To realize a definite gas scale of temperatures it is necessary to take into account the fact that no actual gas thermometer quite fulfills the conditions laid down above. The volume always changes somewhat with changing temperature and pressure, and there is always some gas in the capillary and other pressure-transmitting volume [6] that is not in general at the same temperature as the gas in the thermometer bulb. These facts make it necessary to work with the product pV in place of the single variable p of eq 1. Referring to unit mass of gas, consider the equation

$$pv = aT_g \qquad (2)$$

For any given value of v this may be made identical with eq 1 by making $a/v = c$, so that there are exactly 100° between the ice and steam points. If a is kept fixed while v is allowed to vary, the T_g corresponding to a given thermal state is no longer uniquely defined by eq 2, but may range over a narrow band of values whose width is proportional to the deviation of the gas from Boyle's law. Evidently the ice-to-steam interval will in general be 100° only for one particular gas density. Let a be so chosen that the particular density for which this occurs is the same as the density [7] of the gas in the bulb of a constant-volume gas thermometer. Then, if the total volume of the gas thermometer is V and the mass of gas contained is m, we have

$$pV = maT_g \qquad (3)$$

if the entire thermometer is at uniform temperature. If it is not at uniform temperature, imagine it subdivided into smaller volumes, each of which may be considered to be at uniform temperature. For the gas in each we may write

$$pV_i = m_i aT_{gi}, \qquad (4)$$

[5] H. F. Mueller, J. Research NBS. (Publication pending.)

[6] Other expressions used for this volume are "obnoxious volume", "noxious volume", "dead space", "entrance volume", "unheated space", "schädlicher Raum", and "espace nuisible". The expression "pressure-transmitting volume" was adopted as being more descriptive of the actual function of this part of the apparatus.

[7] This density will change slightly as the thermometer bulb expands and as the temperature of the pressure-transmitting volume changes. Within the experimental error, however, a constant value of a may be used, since the density variations are small.

and summing over all the volumes

$$p\sum_i \frac{V_i}{T_{gi}} = a\sum_i m_i = A = \text{constant}.$$

Separating out and dropping subscripts on the important term which refers to the gas-thermometer bulb,

$$p\left\{\frac{V}{T_g} + \sum_i{}' \frac{V_i}{T_{gi}}\right\} = A, \tag{5}$$

the prime indicating that one of the terms has been taken outside the summation. Variations in the bulb volume may be taken into account by writing

$$\begin{aligned} V &= V_0(1+\alpha T+\beta T^2+ \ldots . +\gamma p+\epsilon p^2+ \ldots .) \\ &= V_0[1+f(T,p)], \end{aligned}$$

the constants being determined by preliminary investigations. Substituting this expression in eq 5 and multiplying by T_g/V_0, we obtain

$$p\left\{1+f(T,p)+\frac{T_g}{V_0}\sum_i{}' \frac{V_i}{T_{gi}}\right\} = \frac{A}{V_0}T_g$$

and putting $V_0/A = C$,

$$T_g = C\left\{1+f(T,p)+\frac{T_g}{V_0}\sum_i{}' \frac{V_i}{T_{gi}}\right\}p. \tag{6}$$

From this equation, T_g may readily be found by successive approximations since only the first term in the braces is large. In the calculations it is generally permissible to use T_g for T in finding the change in bulb volume with temperature. The change in bulb volume with pressure is in many cases negligible. The pressure-transmitting volumes, V_i, must be found by actual measurement, but their change with temperature and pressure may ordinarily be neglected. The temperatures T_{gi} which should be assigned to the transmitting volumes are really defined by eq 4. However, they are ordinarily measured with thermometers or thermocouples calibrated to give temperatures in approximate agreement with the thermodynamic scale. With data on the deviation of the gas from Boyle's law one may calculate how the value of T_{gi} corresponding to a given thermal state will vary as the gas density is changed. For most gases this variation is small, seldom more than a few hundredths of a degree throughout the range of densities likely to occur in a gas-thermometer system. Hence, since the T_{gi}'s occur only in small correction terms, it is generally permissible to replace them directly with the thermometer and thermocouple indications of T.

Experimental determination of the constant C requires in principle that p be measured at both the ice and steam points. In many instances it is better to determine C from measurements made at a single point, employing the results of earlier investigations to insure the preservation of the 100° ice-to-steam interval. With the apparatus used in the present work, for example, determination of C at the oxygen point rather than at the ice and steam points permitted the

helium density to be increased by a factor of 373/90, with a proportional increase in sensitivity. It is worth-while to emphasize that when C is determined without measuring the ice-to-steam interval, the gas-scale temperature, T_g, rather than the thermodynamic temperature, T, of the calibration point must be inserted in eq 6.

To obtain centigrade gas-scale temperatures from temperatures on the corresponding absolute gas scale, the temperature of the ice point on the latter scale must be subtracted,

$$t_g = T_g - T_{g0}.$$

Since many investigators employ the pressure coefficient β and compute temperatures directly on a centigrade gas scale it should be pointed out that in eq 1

$$c = \beta p_0$$

IV. REDUCTION TO THE THERMODYNAMIC SCALE

The most common method of reducing gas-scale temperatures to the thermodynamic scale is based on the assumption that when a gas is used at lower and lower densities, the corresponding gas scale approaches the thermodynamic. Data for helium which permit this extrapolation to zero density have been obtained both at the Reichsanstalt and at Leiden for the temperature range in which we are interested, and tables of corrections [8], [9] based on these data have been published. These corrections are for a centigrade gas scale and are consequently zero at the ice and steam points. To permit a more direct comparison of the results of the two laboratories, the corrections which they would obtain for the absolute scale of the same gas were computed. The Kelvin and Celsius thermodynamic scales satisfy the relation $T = T_0 + t$, while two corresponding gas scales satisfy the relation $T_g = T_{g0} + t_g$. Hence

$$T - T_g = (T_0 - T_{g0}) + (t - t_g). \tag{7}$$

The published tables referred to give values of $t - t_g$.

From the Reichsanstalt data we have computed $T - T_g$ directly, following the procedure of Henning [10] on page 174. In place of his equation for $t - t_s$ ($t - t_g$ in our notation) the corresponding equation

$$T - T_g = -\frac{T}{A_0}\left[(B_t - B_0) - \frac{T_0 + 100}{100}(B_{100} - B_0)\right] p_0$$

was used, where A_0, B_t, etc., are taken from equations of isotherms of the form

$$\frac{(pV)_t}{(pV)_s} = A_t + B_t p + C_t p^2 \ldots\ldots$$

The B values used were computed from the equation used by Henning.[11] The value found for $T_0 - T_{g0}$ was $-0.021°$. As a check,

[8] F. Henning, Z. ges. Kälte-Ind. **37**, 169 (1930).
[9] W. H. Keesom and W. Tuyn, Leiden Commun. Supp. No. 78, table on p. 49. (Reprinted from Travaux et Mémoires du Bureau International des Poids et Mesures **20** (1936).)
[10] Footnote 8.
[11] F. Henning, Z. ges. Kälte-Ind. **37**, 169 (1930); the entire set of constants is given by J. Otto, Hand. Exp. Physik 8, part 2, 191 (1929).

$t-t_g$ was computed from eq 7, using this value, and the values found were identical with those of the Reichsanstalt table.

Keesom and Tuyn plotted the corrections computed from several sets of isotherm data, and based their table on a smooth curve drawn through these points. In the heading of their table it is stated that

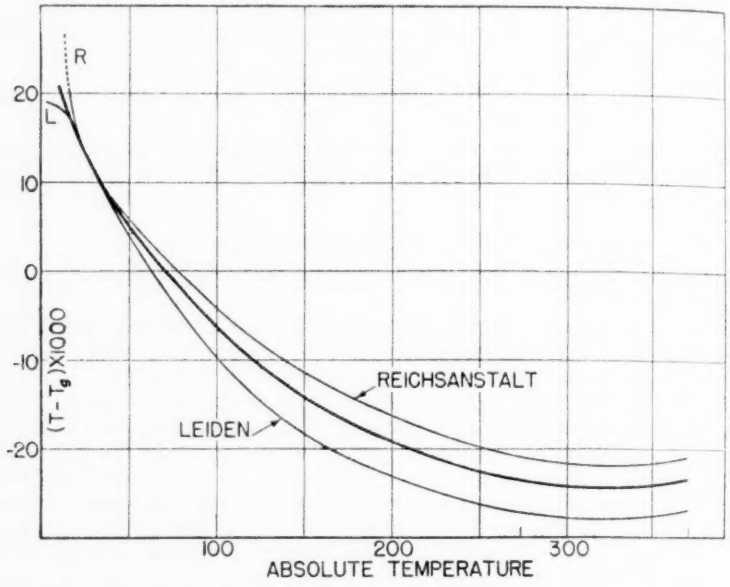

FIGURE 2.—*Corrections for reducing to the thermodynamic scale, computed from data of the Kamerlingh Onnes Laboratory at Leiden and the Physikalisch-Technische Reichsanstalt.*

The heavy line represents corrections adopted for use in this paper.

their corrections are based on a value of -0.361×10^{-6} for $\alpha_A-\alpha_{aHe}$ ($=\gamma-\beta$ in our notation).

Since $T_0=1/\gamma$ and $T_{g0}=1/\beta$, we have

$$(T_0-T_{g0})=1/\gamma-1/\beta=\frac{\beta-\gamma}{\beta\gamma}\doteq T_0^2(\beta-\gamma).$$

Substituting their value for $\beta-\gamma$, we find $T_0-T_{g0}=-0.027°$. This quantity was used with eq 7 to compute $T-T_g$ from the Leiden table.

In table 1 the original values of the two laboratories are reproduced, together with the derived values of $T-T_g$. In figure 2 the corrections $T-T_g$ have been plotted against the absolute temperature. The heavy line on this graph is a weighted mean of the two sets, and represents the corrections adopted for use in the present work. The numerical values are given in table 2. Since the computed ice point pressure of our thermometer was 2.46 m Hg, the corrections actually used were 2.46 times those given in the table.

TABLE 1.—*Deviation of the constant-volume helium gas scale ($p_0=1$ m Hg) from the thermodynamic scale, according to the Kamerlingh Onnes Laboratory at Leiden and the Physikalisch-Technische Reichsanstalt*

t	$T=t+273.16$	$t-t_g$		$T-T_g$	
		L[a]	PTR[b]	L	PTR
100	37.16	0.000	0.000	−0.027	−0.021
50	323.16	−.001	(−.001)	−.028	−.022
0	273.16	.000	.000	−.027	−.021
−50	223.16	.002	.003	−.025	−.018
−100	173.16	.006	.007	−.021	−.014
−150	123.16	.013	.013	−.014	−.008
−180	93.16	.019	.....	−.008	.....
−183	90.16	.....	.019	.....	−.002
−200	73.16	.024	.022	−.003	.001
−220	53.16	.030	(.026)	.003	.005
−240	33.16	.037	(.031)	.010	.010
−250	23.16	.041	.035	.014	.014
−260	13.16	.045	(.045)	.018	.024
−270	3.16	.046	.....	.019	.....

[a] W. H. Keesom and W. Tuyn, Leiden Commun. Supp. No. 78, table on p. 49 (Reprinted from Travaux et Mémoires du Bureau International des Poids et Mesures **20** (1936).
[b] F. Henning, Z. ges. Kälte-Ind. **37**, 169 (1930). Values in parentheses were computed by the authors from Henning's formula.

TABLE 2.—*Deviations used in this paper for correcting from the helium gas scale (T_g) to the thermodynamic (T)*

[For $p_0=1$ m Hg.]

T	$T-T_g$	T	$T-T_g$	T	$T-T_g$	T	T_g
10	+0.021	60	+0.002	120	−0.010	220	−0.021
15	+.018	65	+.001	130	−.012	230	−.021
20	+.016	70	+.000	140	−.013	240	−.022
25	+.013	75	−.001	150	−.014	250	−.022
30	+.011	80	−.002	160	−.015	260	−.023
35	+0.009	85	−0.003	170	−0.016	273.16	−0.023
40	+.008	90	−.004	180	−.017	373.16	−.023
45	+.006	95	−.005	190	−.018	.....	.....
50	+.005	100	−.006	200	−.019	.....	.....
55	+.004	110	−.008	210	−.020	.....	.....

V. PROCEDURE AND CALCULATIONS

The thermometer was filled to approximately atmospheric pressure at liquid-air temperature. The gas was admitted through the manometer after evacuating the system for several days. During the filling the helium was purified by slow passage over charcoal cooled by liquid air and through a cotton-filled tube immersed in liquid hydrogen. Mercury was brought up into the manometer and the manometer tube evacuated. The cryostat was filled with liquid hydrogen and the bulb cooled to the temperature of the hydrogen bath. Measurements were then made at intervals of a few degrees, one operator being required to control the bulb temperature, a second to measure resistances, and a third to observe the pressure. Pressure readings were alternated with resistance-thermometer readings, and the temperature computed from the mean observed pressure. Two thermometers on the mercury column and the thermocouples on the capillary were also read at each temperature. Readings at the

very lowest temperatures were obtained with helium in the space surrounding the bulb.

The pressure readings were corrected for capillarity and reduced to mm Hg at 0° C and standard gravity. Values of R and of $w(=R/R_0)$ for each thermometer were computed. Thermal expansion of the copper thermometer bulb was calculated from the data of Keesom, Van Agt, and Jansen.[12] The equation $V=V_0(0.991171+3.267\times10^{-6}T+1.064\times10^{-7}T^2)$ was found to fit these data satisfactorily below 90° K.[13] A rough calculation showed that pressure changes should have a negligible effect on the volume of the bulb.

The temperatures of the pressure-transmitting volumes were deduced from the thermocouple and thermometer readings. The transmitting volumes were determined by substituting for the gas-thermometer bulb a calibrated glass tube sealed to the capillary and arranged to be filled with mercury to any desired height. After admitting a small amount of gas to the system its volume was varied by changing the height of the mercury in the glass tube. The effect of volume change on the pressure was noted, and the transmitting volume computed from Boyle's law. This process was repeated after cutting off all except a small section of the capillary. Volumes found were 0.180 cm^3 for the space where the capillary joined the manometer, and 0.000942 cm^3/cm length for the capillary. The length of the capillary was 146.7 cm, making the total transmitting volume[14] 0.318 cm^3, or 1.6 percent of the volume of the thermometer bulb, which was 19.69 cm^3. In calculating the quantity

$$\sum_i {}' \frac{V_i}{T_{gi}},$$

a linear change in temperature between one thermocouple and the next was assumed. The section of the capillary between the bulb and the first thermocouple was wound with a heater extending about half its length, by means of which the flow of heat away from the bulb was prevented. A parabolic temperature distribution in the heated section and a linear distribution beyond it were assumed.

To determine the gas-thermometer constant, C, of eq 6 several observations in the neighborhood of the oxygen point were made at the end of each run. All of the thermometers used were intercompared before the final calculations were made, and all had had their oxygen-point resistances determined on the International Temperature Scale. By utilizing the results of the intercomparisons, the error in the oxygen-point resistance assigned to any particular thermometer was considerably reduced. From resistance measurements, the temperatures of all experimental points above 86° K were computed on the International Temperature Scale, on which the boiling point of oxygen is −182.97° C. These were converted to absolute thermodynamic temperatures by using the value of 273.16° K for the thermodynamic temperature of the ice point. Each value of T thus found was converted to the corresponding T_g on the gas

[12] W. H. Keesom, F. P. G. A. J. van Agt, and Miss A. F. J. Jansen, Leiden Commun. 182a (1926).

[13] Southard and Milner (J. Am. Chem. Soc. **55**, 4384 (1933)) used a different equation based on these same data. Dr. Southard has informed us that an error was made in the derivation of their equation.

[14] Earlier estimates of the transmitting volume based on filling a section of the capillary with water and weighing, and computing the volume at the manometer from dimensions gave somewhat smaller values. The possibility that this might be the case was brought to our attention by J. A. Beattie of the Massachusetts Institute of Technology, who also suggested the method finally adopted.

scale by use of table 2 and substituted in eq 6 to determine C. Determined in this way the constant C is presumably the same as would have been obtained by making actual measurements at the ice and steam points. On one occasion during an interruption of measurements the thermometer bulb was kept at liquid-air temperature for more than a month. In this interval the gas in the thermometer was lost at the rate of about 11 parts in 10^6 per day. During a single run such a loss would be entirely negligible, but for each run the value of C was independently determined. Having found C, temperatures were computed from eq 6 and corrected from the gas scale to the thermodynamic by means of table 2. The corrected temperatures and the corresponding resistance values are given in table 3.

TABLE 3.—*Experimental data: p is corrected pressure* ($=T_0/C$ *in eq 6*); *T is temperature corrected from the gas scale to the thermodynamic,* $w=R/R_0$

Point Number	p	T	w_{Z4}	w_{Z11}	w_{M1}
	mm Hg	° *K*			
55	96.16	10.754	0.00 2890	0.00 2952	
18	97.38	10.833	2899	2963	0.55 3710
49	97.68	10.923	2911	2975	
50	100.73	11.262	2963	3026	
56	101.01	11.293	2968	3034	
51	104.91	11.726	0.00 3045	0.00 3110	
52	111.65	12.475	3183	3250	
66	125.48	14.013	3554	3624	
53	125.50	14.015	3561	3630	
67	128.47	14.344	3654	3726	
54	132.18	14.756	0.00 3786	0.00 3860	
68	133.44	14.897	3833	3907	
69	142.69	15.925	4215	4296	
70	153.39	17.115	4751	4827	
57	162.07	18.080	5257		
19	165.07	18.317	0.00 5392		
58	178.10	19.862	6413		
20	182.01	20.191	6656		
11	183.90	20.399	6820	0.00 6917	0.55 5783
71	189.77	21.159	7443	7545	
59	195.82	21.832	0.00 8048	0.00 8154	
21	207.46	23.004	9199	9311	
29	209.63	23.246	9452		
72	235.19	26.209	0.01 3173	.01 3306	
12	245.95	27.261	.01 4731	.01 4870	0.56 0052
22	255.39	28.305	0.01 6464		
30	259.35	28.742	.01 7196	0.01 7350	0.56 1343
13	300.49	33.293	.02 6275		
60	310.12	34.540	.02 9302	.02 9482	
31	315.83	34.990	.03 0330		
23	341.45	37.825	0.03 7719	0.03 7918	.57 1665
14	350.92	38.873	.04 0656	.04 0859	.57 3094
32	360.42	39.925	.04 3731		
73	384.41	42.804	.05 2674	.05 2894	
33	409.93	45.401	.06 1177	.06 1400	.58 2312
24	422.69	46.813	0.06 6058		
34	444.94	49.274	.07 4875		
25	492.10	54.494	.09 4634	0.09 4875	.59 8528
15	499.15	55.274	.09 7631		
35	501.94	55.582	.09 8819		
36	545.03	60.349	0.11 7946	0.11 8188	.60 9276
3	552.65	61.192	.12 1407		
26	575.85	63.759	.13 2076		
A	585.30	64.757	.13 6290		
61	589.95	65.666	.14 0019	.14 0268	
4	595.93	65.982	0.14 1363		
37	623.18	68.997	.15 4157		
B	625.85	69.242	.15 5179		
5	634.51	70.251	.15 9402		
16	640.70	70.936	.16 2422		
42	642.17	71.442	0.16 4606		
C	663.56	73.413	.17 2996		
27	668.81	74.047	.17 5691		
6	690.46	76.443	.18 5968		
D	703.23	77.799	.19 1822		

TABLE 3.—*Experimental data: p is corrected pressure (= T_0/C in eq 6); T is temperature corrected from the gas scale to the thermodynamic, $w = R/R_0$*—Continued

Point Number	p	T	w_{14}	w_{13}	w_{10}
	mm Hg	° K			
38	708.31	78.418	0.19 4514	0.19 4754	0.64 4310
7	713.11	78.949	.19 6776		
65	711.44	79.182	.19 7745	.19 7988	
E	740.89	81.963	.20 9845		
8	751.93	83.245	.21 5384		
I	764.94	84.623	0.22 1438		
44	761.59	84.722	.22 1820		
46	766.03	85.216	.22 3866		
F	778.92	86.169	.22 8058		
1	785.20	86.927	.23 1366	0.23 1608	0.66 1310
J	791.41	87.549	0.23 4078		
9	791.14	87.584	.23 4294		
17	802.95	88.891	.23 9819	0.24 0049	
62	804.91	89.581	.24 2940	.24 3173	
74	809.30	90.069	.24 4956	.24 5187	
40	814.46	90.165	0.24 5425	0.24 5658	0.66 7312
10	815.08	90.233	.24 5762		
41	815.33	90.261	.24 5943	.24 6176	.66 7748
47	812.68	90.403	.24 6420	.24 6651	
G	817.59	90.445	.24 6544		
63	813.70	90.559	0.24 7128	0.24 7358	
28	818.48	90.610	.24 7330	.24 7560	
48	816.44	90.821	.24 8287	.24 8518	
2	823.01	91.111	.24 9465	.24 9696	0.66 9355
64	820.82	91.350	.25 0600	.25 0831	
45	821.56	91.390	0.25 0793	0.25 1025	
39	825.77	91.416	.25 0772	.25 1004	0.66 9949

VI. DATA AND RESULTS

The constants of the seven resistance thermometers are given in table 4. All except two had previously received complete calibrations on the International Temperature Scale. The constants δ and β are those appearing in the modification of Callendar's equation proposed by Van Dusen [15]

$$t = \frac{1}{\alpha}(w-1) + \delta\left(\frac{t}{100}-1\right)\frac{t}{100} + \beta\left(\frac{t}{100}-1\right)\left(\frac{t}{100}\right)^3,$$

which is equivalent to the International Temperature Scale equation and somewhat easier to use.

TABLE 4.—*Constants of the seven calibrated resistance thermometers*

Thermometer	Material	R_0	δ	β	R/R_0 at various fixed points				
					n-H_2, triple (13.96° K)	n-H_2, nbp (20.39° K)	O_2, nbp (90.19° K)	Steam (373.16° K)	Sulfur (717.76° K)
		Ohms							
L8	Pt	29.11355	1.4951	0.11294	0.00 3665	0.00 6993	0.24 6325	1.39 1177	2.64 9570
L5	Pt	23.10284	1.4974	.11142	3669	6990	6114	1316	2.65 0018
L6	Pt	28.83022			3543	6811	5540		
L9	Pt	27.54587	1.4963	.10840	3607	6901	5780	1607	1312
L10	Pt	24.93025	1.4945	.11235	3628	6935	5936	1406	0568
L11	Pt	27.52747	1.4952	.10895	3613	6909	5771	1604	1374
M1	90Pt: 10Ikh	59.47388							

[15] M. S. Van Dusen, J. Am. Chem. Soc. **47**, 326 (1925).

Of the seven resistance thermometers, three (*L6*, *L11*, *M1*) were compared directly with the gas thermometer, and the data given in table 3 obtained. After this the capillary was removed and thermometers *L3*, *L5*, *L9*, and *L10* placed with *L6* in the copper thermometer bulb, which now served as a comparison block. Resistance readings on all the thermometers were then made at 1- or 2-degree intervals throughout the range 10° to 90° K, without making use of the apparatus as a gas thermometer.

No satisfactory simple formula connecting the resistance of platinum and the temperature in this range has yet been proposed. The formula of Henning and Otto [16] based on the sum of two Debye functions can be used, but since it does not avoid the use of a tabulated function it was decided to construct directly a table which gave the resistance-temperature relation for one of the thermometers used (*L6*), and to use this table for the other thermometers by tabulating the

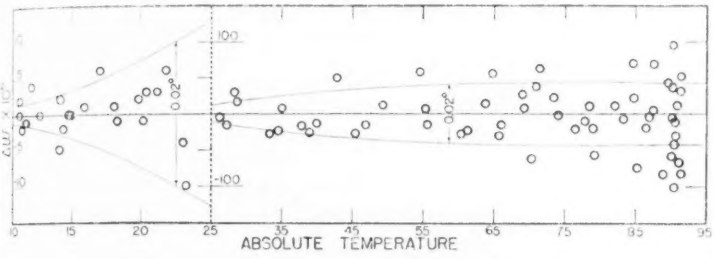

Figure 3.—*Scattering of the experimental points.*

Zero deviation represents agreement with table 5.

deviations of each from this table. A previously published table [17] was taken as a starting point and values of $w(=R/R_0)$ corresponding to the observed temperatures computed from it. These were subtracted from the observed values of W_{L6} and the quantities $(W_{L6}-W_{table})$ plotted. A deviation curve was drawn and used to improve the original table. This process was repeated several times until a table was obtained from which the deviations were random. This table was next smoothed by Spencer's method.[18] The smoothed values are given in table 5, page 364. In figure 3 the deviations of the observed values from this smoothed table are plotted. The curved lines in this graph correspond to $\pm 0.01°$ and allow the scattering to be estimated in degrees. They also show how very rapidly dw/dT falls off below 25° K. It is this rapid decrease which makes it more convenient to plot Δw, which approaches zero, than ΔT, which becomes large. However, the actual scattering is chiefly due to errors in the determination of T rather than w.

[16] F. Henning and J. Otto, Phys. Z. **37**, 601 (1936) and earlier papers.
[17] J. C. Southard and R. T. Milner, J. Am. Chem. Soc. **55**, 4384 (1933).
[18] E. T. Whittaker and G. Robinson, The Calculus of Observations, 2d ed. p. 290 (Blackie and Son, Ltd., London and Glasgow, 1929).

TABLE 5.—*Smoothed temperature-resistance table for platinum, based on thermometer L6*

[$w = R/R_0$. Differences are for use in Bessel's interpolation formula. Example: $w_{55.300} = 10^{-4}\left[96552 + 0.8\left(3931 + \frac{0.8(0.8-1)}{4} \times 75\right)\right] = 0.090694$]

T	w			T	w			T	w		
10	0. 002789			39	0. 041046			67	0. 145672		
		135	59			2921	186			4230	25
11	2924			40	. 043967			68	. 149902		
		166	73			3011	176			4242	22
12	3090			41	. 046978			69	. 154144		
		208	91			3097	169			3252	20
13	3298			42	. 050075			70	. 158396		
		257	105			3180	162			4262	18
14	3555			43	. 053255			71	. 162658		
		313	119			3259	154			4270	16
15	3868			44	. 056514			72	. 166928		
		376	132			3334	147			4278	16
16	4244			45	. 059848			73	. 171206		
		445	146			3406	141			4286	14
17	4689			46	. 063254			74	. 175492		
		522	160			3475	133			4292	14
18	5211			47	. 066729			75	. 179784		
		605	175			3539	125			4300	13
19	5816			48	. 070268			76	. 184084		
		697	187			3600	118			4305	11
20	6513			49	. 073868			77	. 188389		
		792	197			3657	112			4311	12
21	7305			50	. 077525			78	. 192700		
		894	208			3712	104			4317	10
22	8199			51	. 081237			79	. 197017		
		1000	219			3761	97			4321	10
23	9199			52	. 084998			80	. 201338		
		1113	227			3809	91			4327	9
24	0. 010312			53	. 088807			81	. 205665		
		1227	231			3852	84			4330	...
25	. 011539			54	. 092659			82	. 209995		
		1344	235			3893	79			4334	...
26	. 012883			55	. 096552			83	. 214329		
		1462	239			3931	75			4337	...
27	. 014345			56	. 100483			84	. 218666		
		1583	241			3968	70			4339	...
28	. 015928			57	. 104451			85	. 223005		
		1703	240			4001	66			4342	...
29	. 017631			58	. 108452			86	. 227347		
		1823	241			4034	63			4344	...
30	. 019454			59	. 112486			87	. 231691		
		1944	240			4064	58			4344	...
31	. 021398			60	. 116550			88	. 236035		
		2063	237			4092	55			4342	...
32	. 023461			61	. 120642			89	. 240377		
		2181	234			4119	51			4339	...
33	. 025642			62	. 124761			90	. 244716		
		2297	228			4143	48			4336	...
34	. 027939			63	. 128904			91	. 249052		
		2409	222			4165	42			4333	...
35	. 030348			64	. 133069			92	. 253385		
		2519	217			4185	36			4330	...
36	. 032867			65	. 137254			93	. 257715		
		2626	209			4201	32			4327	...
37	. 035493			66	. 141455			94	. 262042		
		2728	199			4217	29			4323	...
38	. 038221							95	. 266365		
		2825	193								

Spencer's method of smoothing does not yield values at the extreme ends of the table. At the upper end of the table the International Temperature Scale supplied the missing values. At the lower end use was made of the equation $R=A+BT^2+CT^5$ proposed by Landau and Pomerantschusk [19] and also by Baber.[20] These authors point out that the term in T^2 should be important in metals such as platinum, which have incomplete inner shells of electrons. This equation fits the experimental data for thermometer *L6* very well up to 15° K, but above this temperature the deviations rapidly become large. Values of the constants found for thermometer *L6* were

$$A=0.067238$$
$$B=1.04350\times10^{-4}$$
$$C=2.74577\times10^{-8}.$$

With this set of constants the T^5 term is negligible below about 5° K and reaches 90 percent of the T^2 term at 15° K. The range in which the equation was used (10° to 15° K) is too small to provide a thorough test, although it does represent a change of 50 percent in absolute temperature. However, it was considered sufficiently good to be used to extend the table down to the lowest temperature measured.

The results of the intercomparison of the various resistance thermometers are shown in figure 4, where the differences $\Delta w_i=w_i-w_{L6}$ have been plotted against the absolute temperature (the index i refers to any one of the calibrated platinum thermometers). From the original large-scale graphs, values of Δw_i were read off at every degree. These values, taken with table 5, are equivalent to a separate table for each platinum thermometer, all agreeing among themselves to within the accuracy of the resistance measurement. Since, except at the lowest temperatures, the precision of the resistance thermometry was of the order of ten times the precision of the gas thermometry, the additional step of intercomparison introduced little additional error. Tables of Δw_i have not been included, since they are useful only in conjunction with a particular group of thermometers.

The 90Pt:10Rh thermometer *M1* cannot be used with table 5. Figure 5 shows the temperature dependence of the resistance of *M1*, after subtracting a constant resistance of 32.5 ohms. The lower curve represents the resistance of the pure platinum thermometer *L6*. It can be seen that the addition of 10 percent of rhodium corresponds roughly to the addition of a constant resistance of 32.5 ohms to a thermometer such as *L6*. Matthiessen's rule, which may be stated in the form "resistance due to impurity is independent of temperature" is seen to hold even when the amount of rhodium "impurity" is as large as 10 percent.

In resistance thermometry the most common problem is that of computing a temperature from a measured resistance. With table 5 this requires inverse interpolation, which is more difficult than direct interpolation. In addition, linear interpolation is insufficiently accurate in this table below 80° K, according to the usual rule that second differences should not exceed 4. Accordingly, table 6, page 366, was made up, the values being found from table 5 by quadratic interpolation. Entries in this table are so closely spaced that linear interpolation introduces no error greater than 0.0005° above 19° K and no error greater than the equivalent of ½ unit in the last figure of w below this temperature.

[19] L. Landau and I. Pomerantschusk, Phys. Z. Sowjetunion **10**, 649 (1936).
[20] W. G. Baber, Proc. Roy. Soc. (London) [A] **158**, 383 (1937).

TABLE 6.—*Resistance-temperature table arranged for linear interpolation. Based on platinum thermometer L6*

[Linear interpolation yields temperatures correct to the nearest 0.001° above 19° K, and correct to the equivalent of the nearest unit in the last figure of w below this temperature. $w = R/R_0$]

W	T	$\frac{\Delta T}{\Delta w}$	W	T	$\frac{\Delta T}{\Delta w}$	W	T	$\frac{\Delta T}{\Delta w}$
0. 002800	10. 090		0. 004500	16. 595		0. 007800	21. 568	
		7780			2170			1160
2850	10. 479		4600	16. 812		7900	21. 678	
		7160			2110			1090
2900	10. 837		4700	17. 023		8000	21. 787	
		6700			2030			1080
2950	11. 172		4800	17. 226		8100	21. 895	
		6260			1970			1060
3000	11. 485		4900	17. 423		8200	22. 001	
		5860			1910			1050
3050	11. 778		5000	17. 614		8300	22. 106	
		5520			1860			1040
3100	12. 054		5100	17. 800		8400	22. 210	
		5160			1800			1030
3150	12. 312		5200	17. 980		8500	22. 313	
		4880			1770			1010
3200	12. 556		5300	18. 157		8600	22. 414	
		4640			1710			1010
3250	12. 788		5400	18. 328		8700	22. 515	
		4420			1680			990
3300	13. 009		5500	18. 496		8800	22. 614	
		4220			1630			980
3350	13. 220		5600	18. 659		8900	22. 712	
		4040			1600			970
3400	13. 422		5700	18. 819		9000	22. 809	
		3880			1560			
3450	13. 616		5800	18. 975				
		3720			1530			
3500	13. 802		5900	19. 128		0. 009000	22. 809	
		3600			1490			960
3550	13. 982		6000	19. 277		9200	23. 001	
		3480			1470			935
3600	14. 156		6100	19. 424		9400	23. 188	
		3360			1430			920
3650	14. 324		6200	19. 567		9600	23. 372	
		3260			1410			905
3700	14. 487		6300	19. 708		9800	23. 553	
		3160			1390			885
3750	14. 645		6400	19. 847		0. 010000	23. 730	
		3060			1350			870
3800	14. 798		6500	19. 982		. 010200	23. 904	
		2980			1340			855
3850	14. 947		6600	20. 116		. 010400	24. 075	
		2900			1320			840
3900	15. 092		6700	20. 248		. 010600	24. 243	
		2840			1290			830
3950	15. 234		6800	20. 377		. 010800	24. 409	
		2740			1270			815
4000	15. 371		6900	20. 504		. 011000	24. 572	
		2700			1250			805
4050	15. 506		7000	20. 629		. 011200	24. 733	
		2620			1240			790
4100	15. 637		7100	20. 753		. 011400	24. 891	
		2580			1210			780
4150	15. 766		7200	20. 874		. 011600	25. 047	
		2500			1200			770
4200	15. 891		7300	20. 994		. 011800	25. 201	
					1180			760
			7400	21. 112		. 012000	25. 353	
					1160			750
0. 004200	15. 891		7500	21. 228		. 012200	25. 503	
		2440			1150			740
4300	16. 135		7600	21. 343		. 012400	25 651	
		2350			1130			730
4400	16. 370		7700	21. 456		. 012600	25. 797	
		2250			1120			720

TABLE 6.—*Resistance-temperature table arranged for linear interpolation. Based on platinum thermometer L6*—Continued

W	T	$\frac{\Delta T}{\Delta w}$	W	T	$\frac{\Delta T}{\Delta w}$	W	T	$\frac{\Delta T}{\Delta w}$
0.012800	25.941		0.022000	31.298		0.039000	38.279	
		710			486			356
.013000	26.083		.022500	31.541		.039500	38.457	
		705			480			354
.013200	26.224		.023000	31.781		.040000	38.634	
		695			474			
.013400	26.363		.023500	32.018				
		690			468			
.013600	26.501		.024000	32.252		0.040000	38.634	
		680			462			350
.013800	26.637		.024500	32.483		.041000	38.984	
		670			456			346
.014000	26.771		.025000	32.711		.042000	39.330	
					452			342
			.025500	32.937		.043000	39.672	
					444			339
0.014000	26.771		.026000	33.159		.044000	40.011	
		663			440			335
.014300	26.970		.026500	33.379		.045000	40.346	
		653			436			332
.014600	27.166		.027000	33.597		.046000	40.678	
		643			432			329
.014900	27.359		.027500	33.813		.047000	41.007	
		637			426			326
.015200	27.550		.028000	34.026		.048000	41.333	
		623			422			323
.015500	27.737		.028500	34.237		.049000	41.656	
		617			418			320
.015800	27.922		.029000	34.446		.050000	41.976	
		607			414			318
.016100	28.104		.029500	34.653		.051000	42.294	
		600			410			314
.016400	28.284		.030000	34.858		.052000	42.608	
		593			408			313
.016700	28.462		.030500	35.062		.053000	42.921	
		587			402			310
.017000	28.638		.031000	35.263		.054000	43.231	
		577			400			307
.017300	28.811		.031500	35.463		.055000	43.538	
		570			396			306
.017600	28.982		.032000	35.661		.056000	43.844	
		567			392			303
.017900	29.152		.032500	35.857		.057000	44.147	
		557			390			301
.018200	29.319		.033000	36.052		.058000	44.448	
		553			386			300
.018500	29.485		.033500	36.245		.059000	44.748	
		547			382			297
.018800	29.649		.034000	36.436		.060000	45.045	
		540			380			296
.019100	29.811		.034500	36.626		.061000	45.341	
		533			378			293
.019400	29.971		.035000	36.815		.062000	45.634	
		530			376			292
.019700	30.130		.035500	37.003		.063000	45.926	
		523			372			290
.020000	30.287		.036000	37.189		.064000	46.216	
					368			289
			.036500	37.373		.065000	46.505	
					368			287
0.020000	30.287		.037000	37.557		.066000	46.792	
		518			364			285
.020500	30.546		.037500	37.739		.067000	47.077	
		508			362			284
.021000	30.800		.038000	37.920		.068000	47.361	
		502			360			283
.021500	31.051		.038500	38.100		.069000	47.644	
		494			358			281

TABLE 6.—*Resistance-temperature table arranged for linear interpolation. Based on platinum thermometer L6*—Continued

W	T	$\frac{\Delta T}{\Delta w}$	W	T	$\frac{\Delta T}{\Delta w}$	W	T	$\frac{\Delta T}{\Delta w}$
0. 070000	47. 925		0. 104000	56. 887		0. 150000	68. 023	
		280			250. 5			235.5
. 071000	48. 205		. 106000	57. 388		. 155000	69. 202	
		278			249. 5			235.0
. 072000	48. 483		. 108000	57. 887		. 160000	70. 377	
		277			249. 0			234.4
. 073000	48. 760		. 110000	58. 385		. 165000	71. 549	
		276			247. 5			233.8
. 074000	49. 036		. 112000	58. 880		. 170000	72. 718	
		275			246. 5			233.4
. 075000	49. 311		. 114000	59. 373		. 175000	73. 885	
		274			246. 0			233.0
. 076000	49. 585		. 116000	59. 865		. 180000	75. 050	
		272			245. 0			232.5
. 077000	49. 857		. 118000	60. 355		. 185000	76. 213	
		272			244. 5			232.2
. 078000	50. 129		. 120000	60. 844		. 190000	77. 374	
		270			243. 0			231.8
. 079000	50. 399		. 122000	61. 330		. 195000	78. 533	
		269			243. 0			231.4
. 080000	50. 668		. 124000	61. 816		. 200000	79. 690	
					242. 0			231.2
0. 080000	50. 668		. 126000	62. 300		. 205000	80. 846	
		268. 0			241. 0			231.0
. 082000	51. 204		. 128000	62. 782		. 210000	82. 001	
		266. 0			241. 0			230.8
. 084000	51. 736		. 130000	63. 264		. 215000	83. 155	
		264. 0			240. 0			230.4
. 086000	52. 264		. 132000	63. 744		. 220000	84. 307	
		262. 5			239. 5			230.4
. 088000	52. 789		. 134000	64. 223		. 225000	85. 459	
		261. 0			239. 0			230.4
. 090000	53. 311		. 136000	64. 701		. 230000	86. 611	
		259. 5			238. 5			230.2
. 092000	53. 830		. 138000	65. 178		. 235000	87. 762	
		258. 0			238. 0			230.2
. 094000	54. 346		. 140000	65. 654		. 240000	88. 913	
		256. 5			237. 5			230.4
. 096000	54. 859		. 142000	66. 129		. 245000	90. 065	
		255. 0			237. 5			230.8
. 098000	55. 369		. 144000	66. 604		. 250000	91. 219	
		254. 5			237. 0			230.8
. 100000	55. 878		. 146000	67. 078		. 255000	92. 373	
		252. 5			236. 5			231.0
. 102000	56. 383		. 148000	67. 551		. 260000	93 528	
		252. 0			236. 0			231.2
			. 150000	68. 023		. 265000	94. 684	

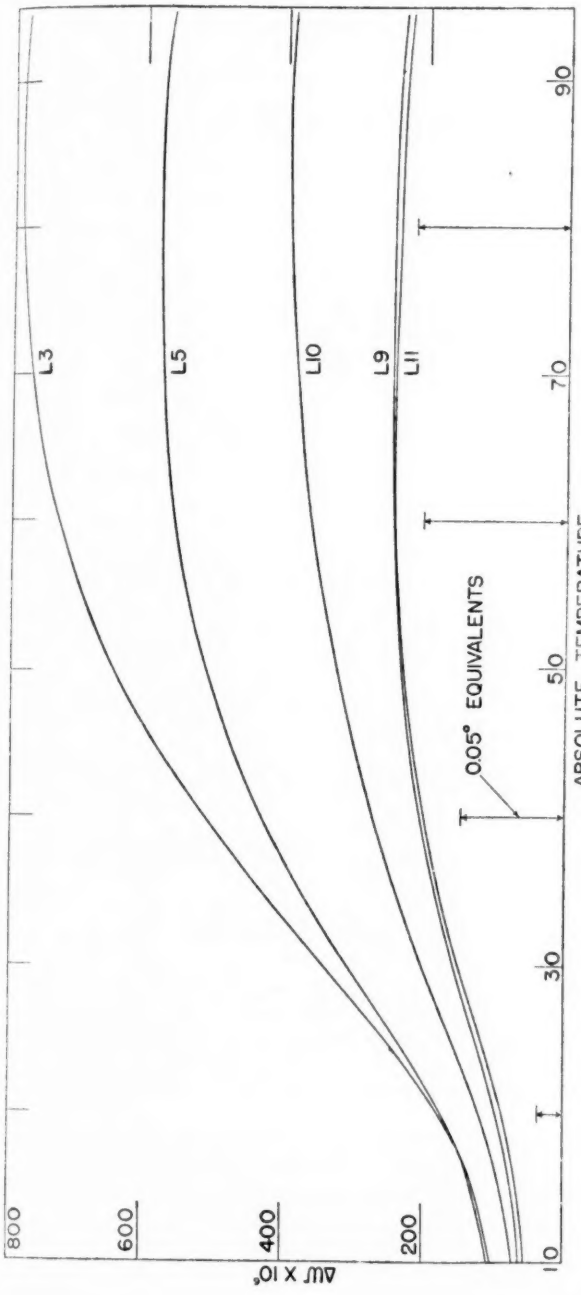

FIGURE 4.—*Comparison of the six calibrated platinum resistance thermometers.*
$\Delta w_1 = w_1 - w_{14}$ and $w = R/R_0$.

After the calibration and intercomparison had been completed, resistance thermometer *L3* was installed in a calorimetric apparatus in which the vapor pressure of hydrogen could be measured, and in which the triple point could be located calorimetrically. Values found for the resistance of *L3* at the triple point and boiling point of normal hydrogen are given in table 4. The resistances of the other thermometers at these fixed points were found by adding the

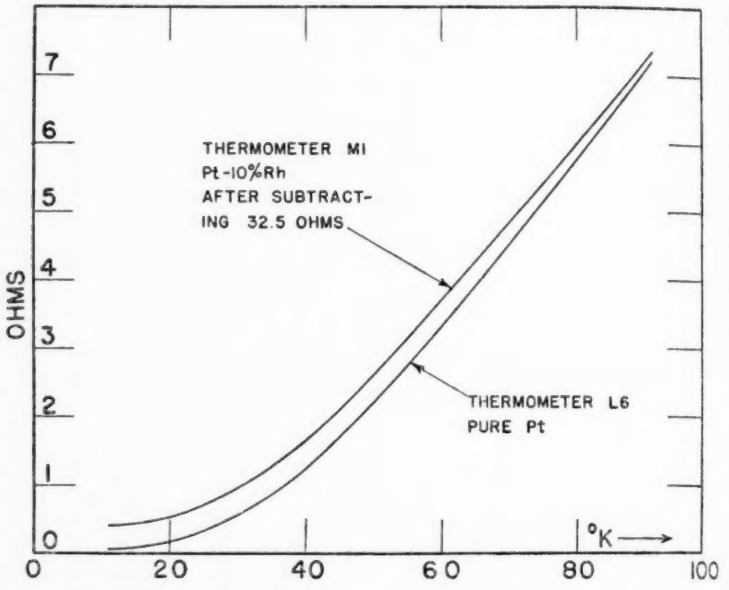

FIGURE 5.—*Temperature dependence of the resistance of pure platinum compared with that of an alloy containing 10 percent of rhodium.*

appropriate values of Δw_t, as determined by the intercomparisons. The temperatures corresponding to these resistances are

triple point—13.96° K
boiling point—20.39° K.

The most recent of the previously reported values for these fixed points are 13.96° K by Henning and Otto [21] for the triple point, and −252.754° C (20.37$_6$° K) by Keesom, Bijl, and Van der Horst,[22] and 20.38° K by Heuse and Otto [23] for the boiling point. A summary of work on low-temperature fixed points has been given by Henning and Otto.[24]

Three years prior to obtaining the above values, thermometer *L3* had been used in an apparatus for determining the vapor pressure of hydrogen, and its resistance at the boiling point of normal hydrogen

[21] F. Henning and J. Otto, Phys. Z. **37**, 601 (1936); **37**, 633 (1936).
[22] W. H. Keesom, A. Bijl, and H. van der Horst, Leiden Commun. 217a (1931). The pressure coefficient used by these authors was 0.0036609, whence T_{g0}=273.157 or using the Leiden value of $T_g - T_{g0}$ in table 1, T_0=273.13. With this value of T_0 the boiling point is 20.37$_6$° K rather than 20.336, the value given in Henning and Otto's summary.
[23] W. Heuse and J. Otto, Ann. Physik **9**, 486 (1931).
[24] F. Henning and J. Otto, Phys. Z. **37**, 633 (1936).

had been determined. The temperature computed from this resistance agreed within slightly less than 0.01° with that given above. This was considered satisfactory, in view of the fact that the two determinations were made with entirely different apparatus and with different resistance thermometers.

VII. ESTIMATION OF ERRORS

Pressure.—Uncertainty in the pressure measurements is responsible for a large part of the scattering of the data. The height of the mercury column could be read on the calibrated glass scale to about 0.1 mm, which is equivalent to about 0.01°. The uncertainty in the temperature of the column was reduced by surrounding it with light aluminum shields, leaving only the two menisci exposed. Even so, it was found necessary on some occasions to circulate the air in the room to keep the top and bottom of the column at the same temperature. Meniscus corrections were made, although the menisci were so regular that they could for the most part have been omitted. Thermal transpiration might be expected to set up a pressure gradient in the capillary. R. B. Scott of this Bureau investigated the effect for helium. His results (unpublished) are in substantial agreement with the theory,[25] and indicate that the pressure at the two ends of the gas-thermometer capillary could not have differed by more than 0.003 mm even under the most unfavorable conditions.

Pressure-transmitting volume.—Errors in the corrections for the pressure-transmitting volume may be due either to errors in the volume ratios V_t/V_0 or to errors in the determination of the temperatures T_t. The temperatures obtained from thermocouple readings were computed from the equation, $\text{emf}=a+bT^2+cT^3+dT^4$, proposed by Ahlberg and Lundberg,[26] the constants being determined by calibration at the boiling and triple points of hydrogen and in liquid air at normal and reduced pressure. Of the V_t the most uncertain was the volume where the capillary joined the manometer. This volume was subject to fluctuation, not only because of the difficulty of setting the mercury meniscus exactly on the tip of the pointer, but also because of variations in meniscus height. In the 11-mm manometer tube used, a change in meniscus height from 1.4 to 1.6 mm would increase the transmitting volume by 14 mm^3 according to data in the International Critical Tables. In our work variations in meniscus height were actually more serious in their effect on the transmitting volume than in their effect on the pressure.

Thermal expansion of bulb.—The change in volume of the copper bulb from 11° K to 90° K calculated from eq 3 is about 0.11 percent. An error of even 4 percent in the mean expansion coefficient over this range would give rise to a maximum error in temperature of only slightly over 0.001°.

Thermometer constant C.—By obtaining the thermometer constant in the particular manner described in the section on procedure and calculations, continuity with the International Temperature Scale is secured. The value 90.19° K accepted for the oxygen point in determining C may be in error either because of uncertainty in the value −182.97° C assigned to the oxygen point on the International Tem-

[25] M. Knudsen, Ann. Physik **83**, 797 (1927).
[26] J. E. Ahlberg and W. O. Lundberg, J. Am. Chem. Soc. **57**, 2722 (1935).

perature Scale or because of uncertainty in the value 273.16° K used for the ice point. Since the error introduced in this way is proportional to the temperature, it will in any case be very small at the lower end of the scale.

Since C is inversely proportional to the mass of gas in the thermometer, any loss of gas from the system or change in the effective mass by adsorption will cause error unless corrected for. The loss by diffusion during a single run was entirely negligible. An estimate of the thickness of the layer of gas which would have to be adsorbed to produce appreciable error led us to conclude that this effect was probably negligible.

Reduction to the thermodynamic scale.—The corrections used to reduce to the thermodynamic scale were taken from the results of other investigators. The error introduced is probably small at the higher temperatures but may be rather important below the boiling point of hydrogen.

VIII. COMPARISON WITH PREVIOUS WORK

Comparison of the temperature scales set up by different laboratories is chiefly a matter of comparing the values assigned to fixed points.

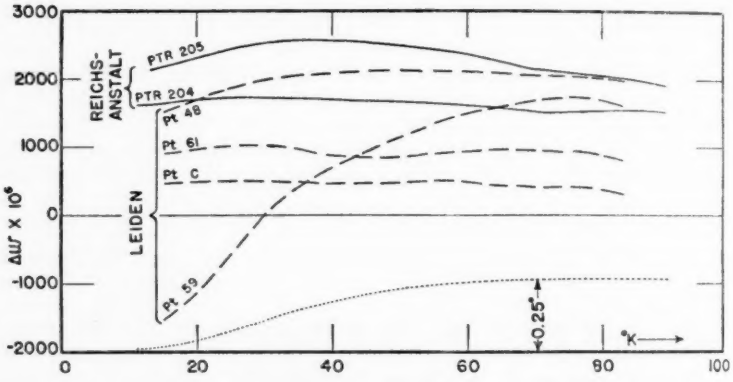

FIGURE 6.—*Comparison of thermometers calibrated by other laboratories with thermometer L6.*

$\Delta w_t = w_t - w_{table}$ and $w = R/R_0$.

However, some additional information may be obtained by combining the data of the different laboratories to obtain graphs similar to figure 4. This is of course only possible when the resistance thermometers are of the same material. Figure 6 is such a graph, utilizing recent results from Leiden [27] and the Reichsanstalt.[28] [29] Taking table 5 as a standard, $\Delta w_t = w_t - w_{table}$ has been plotted against the absolute temperature. It will be seen that the deviations are much larger than those found by intercomparison of our own thermometers. This is probably due chiefly to greater differences in the samples of platinum. However, the deviation curves are not as smooth as those of our own thermometers, and this lack of smoothness is probably associated with

[27] W. H. Keesom and A. Bijl, Physica **3**, 418 (1936). (Leiden Commun. 242b).
[28] F. Henning and J. Otto, Phys Z. **37**, 601 (1936);
[29] F. Henning and J. Otto, Actes 6 ème congr. int. froid (Buenos Aires) **2b**, 257 (pub. 1935).

differences in gas thermometry. It should be emphasized that the choice of a standard table was arbitrary and that if the table of another laboratory were chosen the deviations of our thermometers would show a corresponding lack of smoothness. The 11 thermometers for which Δw_t is plotted in figures 4 and 6 represent platinum from at least three different sources. Such a sampling is too limited to allow any general conclusions to be drawn. However, it is of interest to point out certain characteristics of these 11 thermometers. Since resistance thermometers are supposedly constructed only of platinum of high purity, it is to be expected that their curves of w versus T will be very similar in form. All such curves have a common point at 0° C, and it is evident that if their slopes at this temperature are very nearly equal, values of Δw_t will be small for a considerable distance to either side of 0° C. At low temperatures, however, values of Δw_t may become large, even though the curves may still be nearly parallel. Several of the deviation curves of figures 4 and 6 illustrate this type of behavior. Between 60° and 90° K, for example, the curves of figure 4 are all parallel to the T-axis to within the equivalent of about 0.01°. In figure 6 all the curves except one are approximately parallel to the T-axis. The exception is the Leiden thermometer Pt 59, for which the platinum was prepared [30] by decomposition of $PtCOCl_2$.

The authors acknowledge the assistance of D. O. Burger, who made the resistance thermometers. Their thanks are also due to C. S. Cragoe, to whom they are indebted for valuable discussions.

WASHINGTON, December 20, 1938.

[30] W. H. Keesom and A. Bijl, Physica **3**, 418 (1936) (Leiden Commun. 242b).

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